

REPORT DOCUMENTATION PAGE				Form Approved OMB No. 0704-0188	
<p>The public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing the burden, to Department of Defense, Washington Headquarters Services, Directorate for Information Operations and Reports (0704-0188), 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302. Respondents should be aware that notwithstanding any other provision of law, no person shall be subject to any penalty for failing to comply with a collection of information if it does not display a currently valid OMB control number.</p> <p>PLEASE DO NOT RETURN YOUR FORM TO THE ABOVE ADDRESS.</p>					
1. REPORT DATE (DD-MM-YYYY) 06-09-2003		2. REPORT TYPE Final Technical Report		3. DATES COVERED (From - To) 9/1/2002 - 8/31/2003	
4. TITLE AND SUBTITLE Symposium H: Three-Dimensional Nanoengineered Assemblies				5a. CONTRACT NUMBER	
				5b. GRANT NUMBER N00014-02-1-0775	
				5c. PROGRAM ELEMENT NUMBER	
				5d. PROJECT NUMBER	
6. AUTHOR(S) Koji Ikuta, Nagoya University, Japan Lhadi Merhari, CERAMEC R&D, France Thomas Orlando, Georgia Inst of Technology David P. Taylor, Aerospace Corporation				5e. TASK NUMBER	
				5f. WORK UNIT NUMBER	
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) Materials Research Society 506 Keystone Dr Warrendale PA 15086				8. PERFORMING ORGANIZATION REPORT NUMBER	
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES) Office of Naval Research 800 N Quincy St Arlington VA 22217-5660				10. SPONSOR/MONITOR'S ACRONYM(S) ONR	
				11. SPONSOR/MONITOR'S REPORT NUMBER(S)	
12. DISTRIBUTION/AVAILABILITY STATEMENT Distribution limitation - None					
13. SUPPLEMENTARY NOTES None					
14. ABSTRACT Attached					
20030612112					
15. SUBJECT TERMS					
16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	18. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON
a. REPORT	b. ABSTRACT	c. THIS PAGE			Donna J. Gillespie, Symposium Fund Administrator
N/A	N/A	N/A	None	23	19b. TELEPHONE NUMBER (Include area code) 724-779-3004 Ext 202/gillespie@mrs.org

Standard Form 298 (Rev. 8/98)
Prescribed by ANSI Std. Z39.18

BEST AVAILABLE COPY

2002 MRS Fall Meeting Final Technical Report

The **3D Nanoengineered Assemblies** symposium brought together researchers from a wide range of fields. The conference topic is not focused on a particular area of research, but on a goal that is being pursued by many groups approaching from diverse directions. 3D Nanoengineered Assemblies included much work that was "not quite truly 3D" and "not quite on the nanoscale." The result was a meeting in which common overarching themes emerged from presentations in widely separated research areas. More than 100 abstracts were submitted, and there were 29 invited talks covering work that spanned a remarkable number of topics. The symposium was generally well attended, and there was good feedback about the overall quality of the presentations.

One of the most interesting aspects of nanotechnology is the ability to access physical phenomena that occur on the nanoscale. A compelling example of this sort of nanoscale phenomena exploits the collective electronic excitations (plasma oscillations or plasmons) in metal nanoparticles to manipulate energy and matter. This work was well represented by talks from Harry Atwater (CalTech), Frank Traeger (Kassel), Mostafa El-Sayed (Georgia Tech), Richard Blaike (Canterbury) and Meg Abraham (Aerospace Corp.). In particular, Harry Atwater's talk showed how plasmons in metal particles on a surface could be used to direct the flow of energy in a material analogous to more conventional electronic devices. Other talks demonstrated the use of plasmons to control the size and shape of the metal nanoparticles both on a surface and in the bulk. This is a compelling set of applications for nanotechnology in general and 3D nanoengineered assemblies in particular.

Lithographic methods can be either masked based or mask-less. Much of the time devoted to modern materials processing has been spent developing mask based lithographic techniques and as a consequence they are quite mature. Some of the speakers presented work that used conventional methods at high resolution to great advantage. An example of this sort of work is provided by the presentation of Harold Craighead (Cornell). There were a variety of talks that presented variations on these methods, perhaps best exemplified by Ulrich Goesele's talk (MPI-Halle). Steven Brueck (UNM) presented a talk on laser based interference methods that both argues that the limits to optical methods have not been reached. This connects with lithographic processes because nonlinear response is important both for photo resist materials and for many of the direct write schemes for processing in three dimensions, (such as found in the work of Shoji Marou and Koji Ikuta).

The mask-less direct write processing community was well represented by electron and particle beam talks including those of J. Alex Liddle (LBNL), Hans Loeschner (IMS), and Andrew Bettioli (Nat. U. Singapore). There were also a variety of talks on soft lithographic methods, including John Rogers (Lucent) and Sigurd Wagner (Princeton).

Non-lithographic techniques were also discussed in this meeting. This included a number of talks on self-assembly. Nanoparticle assemblies, Nanotubes, Nanowires and Nanosprings were the topics of a number of talks. Ones that stand out in my memory

are Reg Penner's (UC Irvine) talk on electrochemical methods of producing nanowires, Walt deHeer's (Georgia Tech) and Dave McIlroy's (U Idaho) nanospring talk.

Two of the aspects of the biological model for materials processing that make it most appealing are the directed self-assembly and the bottom-up approach to processing. Together, these aspects of biological control of materials have become a prototype for an elegant approach to processing. If biological processes can be understood and controlled or mimicked, then there is potential to build structures starting on the nanoscale. This approach implicitly offers some level of 3D control from the nanoscale all the way to large structures. A significant part of this work has been directed at carbonates and this was highlighted in an overview talk from Dan Morse (UCSB) and excellent talks from several speakers including Jim deYoreo (LLNL) and Ken Sanhage (Ohio State).

A large number of excellent talks presented interesting work in this symposium. Part of the success of the "3D Nanoengineered Assemblies" symposium is that it touches on a presently topical aspect of research. However, the real strength of this meeting was the multidisciplinary character of the entire symposium. I believe this was evident when a chemist and a physicist who might seldom cross paths gave related talks in the same session. This also happened in the "plasmon processes on the nanoscale" session where the collection of talks told part of a larger story concerning what I think is one of the most interesting examples of the sort of emerging new physics that can be accessed with control of materials on the nanometer scale. The "3D Nanoengineered Assemblies" symposium succeeded in presenting to researchers a snapshot of the current work on this topic, in keeping with the best traditions of the Materials Research Society Meetings.

David P. Taylor
The Aerospace Corporation

SYMPOSIUM H
Three-Dimensional Nanoengineered Assemblies

December 1 – 5, 2002

Chairs

Koji Ikuta

Dept. of Micro System Engineering
Nagoya Univ
Furocho 1
Nagoya, Aichi 464-8603 JAPAN
81-52-789-5024

Lhadi Merhari

CERAMEC R&D France
Limoges, F-87000 FRANCE
33-555-79-4005

Thomas Orlando

School of Chemistry & Biochemistry
Georgia Inst of Technology
1-98 Boggs Bldg
Atlanta, GA 30332-0400
404-894-4012

David P. Taylor

Space Materials Lab
Aerospace Corp
M2-241
El Segundo, CA 90245
310-336-2067

Symposium Support

Air Force Office of Scientific Research
Army Research Office
National Science Foundation
Office of Naval Research

Proceedings to be published in both book form and online
(see *ONLINE PUBLICATIONS* at www.mrs.org)
as Volume 739
of the Materials Research Society
Symposium Proceedings Series

* Invited paper

BEST AVAILABLE COPY

TUTORIAL

FT H: LITHOGRAPHIC AND NONLITHOGRAPHIC METHODS FOR 3D NANOFABRICATION

Sunday, December 1, 2002

2:00 p.m. - 5:00 p.m.

Room 201 (Hynes)

Nanotechnology is considered the key technology of the 21st century and is expected to bring ultimate solutions to current problems. However, among the issues to address to ensure the industrial viability of nanotechnology is the selection of a 3D nanofabrication method that can be scaled up. This tutorial will describe state-of-the-art lithographic and nonlithographic methods and critically compare their performances in fields as diverse as 3D nanostructures, photonic crystals, and electronic devices.

Instructors:

Shinji Matsui, Himeji Institute of Technology

John A. Rogers, Bell Laboratories, Lucent Technologies

SESSION H1: NANOFABRICATION VIA LITHOGRAPHIC TECHNIQUES

Chairs: Lhadi Merhari and David P. Taylor

Monday Morning, December 2, 2002

Room 309 (Hynes)

8:30 AM *H1.1

INTERFEROMETRIC LITHOGRAPHY AND NANOSCALE-PATTERNED SEMICONDUCTOR GROWTH. **S.R.J. Brueck**, Center for High Technology Materials, University of New Mexico, Albuquerque, NM.

Interferometric lithography (IL) provides a facile, large-area, low-cost nanopatterning technique. Using available ultraviolet laser sources, pattern periods as low as ~ 75 nm are possible. Since the limitation in optics is on the period rather than the linewidth, nonlinear interpolation techniques allow extensions to ~ 37 nm and below. Integration of the periodic capabilities of IL with conventional optical lithography to provide isolated areas of nanostructures offers a powerful patterning capability with application in many areas including nanostructured crystal growth, photonic crystals, magnetic materials, molecular electronics and nanostructure-biology interactions. Particular emphasis will be placed on the use of nanostructured substrates for semiconductor crystal growth. Examples will be drawn from MOCVD nanoheteroepitaxy growth of highly mismatched materials (e.g. GaN on Si) and MBE growth of engineered quantum wires and dots in the InAs/GaAs system.

9:00 AM *H1.2

TECHNIQUES AND APPLICATIONS FOR NON-PLANAR LITHOGRAPHY. **John A. Rogers**, Bell Laboratories, Murray Hill, NJ.

Certain specialized techniques for high resolution printing and molding can be used to form micro and nanostructures directly onto non-planar (e.g. rough, curved or multi-leveled) surfaces. This talk describes some of these methods and it gives examples of their use in electronics, photonics and certain areas of biotechnology. In particular, we illustrate how microcontact printing onto cylindrical supports can yield (i) microsprings for MEMS, (ii) conducting microcoils for inductors, transformers and excitation/detection coils for high resolution NMR, and (iii) free-standing metallic microstructures for intravascular stents. This printing approach and a related method for nanomolding also provide direct routes to three dimensional nanostructures (e.g. distributed feedback gratings on the top surfaces of rib waveguides) that are useful as components in integrated optical systems. Finally, we introduce a nanotransfer printing technique that is capable of purely additive, single-step patterning of complex multilayer stacks with near-molecular edge resolution. We illustrate some applications of this method in plastic and molecular electronics.

9:30 AM *H1.3

ION PROJECTION DIRECT-STRUCTURING (IPDS) FOR NANOTECHNOLOGY APPLICATIONS. **Hans Loeschner**, Elmar Platzgummer, and Gerhard Stengl, IMS Nanofabrication GmbH, Vienna, AUSTRIA.

Large-field ion-optics has been developed for reduction and proximity printing [1]. Sub-100nm ion projection direct-structuring (IPDS) of patterned magnetic media discs has been demonstrated within exposure fields of 17mm diameter [2]. Tool development and further

important IPDS nanotechnology applications will be discussed. [1] Hans Loeschner, Gerhard Stengl, et al., Proc. SPIE Vol. 4688, paper 71, t.b.p. July 2002. [2] Andreas Dietzel, Ruediger Berger, et al., Intermag Europe 2002, 28 Apr - 2 May 2002, Amsterdam.

10:30 AM *H1.4

PROTON BEAM MICROMACHINING: A NEW 3D SUB-100 NM DIRECT-WRITE TECHNIQUE. **Frank Watt**, **Jeroen van Kan** and **Andrew Bettiol**, Research Centre for Nuclear Microscopy, Dept of Physics, National University of Singapore, SINGAPORE.

Proton Beam Micromachining (PBM) using MeV protons has the unique capability of producing direct-write high-aspect-ratio 3D structures in resist material. Protons, being 1800 times more massive than electrons, do not suffer from lateral scattering as the protons penetrate the resist and, unlike X-rays, have an almost linear energy deposition with depth (except for a localized increase at the end of range). These features allow smooth, straight walled, high aspect ratio structures to be produced. An added feature is that the depth to which the protons expose the resist can be varied by changing the proton energy, allowing multi-level 3D structures to be created (e.g. a 1 MeV proton beam will penetrate 20 microns into PMMA, whereas a 2 MeV beam will penetrate 61 microns). Investigations taking place in the Research Centre for Nuclear Microscopy, Dept of Physics, National University of Singapore, have shown that the PBM process has high potential for 3D applications in microphotonics, microfluidics, tissue engineering substrates, and is also particularly suited to the rapid production of high quality 3D stamps and molds for soft lithography using polymers. In addition, recent advances in quadrupole lens technology has enabled protons to be focused down to 35 nm spot sizes, enabling sub-100nm 3D structures to be produced.

11:00 AM *H1.5

RESIST REQUIREMENTS AND LIMITATIONS FOR NANOSCALE ELECTRON-BEAM PATTERNING. **J. Alexander Liddle**, Lawrence Berkeley National Laboratory, Berkeley, CA.

Electron beam lithography still represents the most effective way to pattern materials at the nanoscale, especially in the case of structures, which are not indefinitely repeating a simple motif. The success of e-beam lithography depends on the availability of suitable resists. There is a substantial variety of resist materials, from PMMA to calixarenes, to choose from to achieve high resolution in electron-beam lithography. However, these materials suffer from the limitation of poor sensitivity. In both direct-write and projection e-beam systems the maximum beam current for a given resolution is limited by space-charge effects. In order to make the most efficient use of the available current, the resist must be as sensitive as possible. This leads, naturally, to chemically amplified (CA) systems. Unfortunately, in the quest for ever smaller feature sizes and higher throughputs, even chemically amplified materials are limited: ultimately, sensitivity and resolution are not independent. Current resists already operate in the regime of < 1 electron/nm². In this situation discrete models are the only way to understand material performance and limits. In this talk I will describe resist requirements, including sensitivity, etch selectivity, environmental stability, outgassing, and line-edge roughness as they pertain to, high-voltage (100 kV) direct write and projection electron-beam exposure systems. I will present some of the experimental results obtained on CA resists in the SCALPEL exposure system and discuss the fundamental sensitivity limits of CA and conventional materials in terms of shot-noise and resolution limits in terms of e-beam solid interactions.

11:30 AM H1.6

NANOSCALE PATTERNING OF COBALT-COBALT OXIDE INTERFACES. **J.W. Lau**, **Y. Zhu**, Brookhaven National Laboratory, Upton, NY.

A goal of this project is to tailor assemblies of Co/CoO structures for the purpose of studying magnetic behavior between ferromagnetic and antiferromagnetic interfaces. We have successfully patterned periodic structures containing cobalt-cobalt oxide interfaces with electron beam lithography. A 20 nm uniform cobalt film was deposited on both silicon nitride and holey carbon substrates. A 10 nm layer aluminum fluoride film was subsequently deposited as an e-beam resist. The lithography was carried out in a JEOL JEM-3000F transmission electron microscope, with a minimum probe size of 2 Å. Results indicate that feature sizes much below 50 nm are possible. The lithography procedure removes both aluminum and fluorine, leaving behind bare cobalt. Annealing in air oxidizes the exposed cobalt features. Changes in the oxidation state of these cobalt features may be studied with electron energy loss spectroscopy.

11:45 AM H1.7

CHEMICAL NANOLITHOGRAPHY WITH ELECTRON BEAMS. **Wolfgang Eck**, **Armin Götzhäuser**, **Wolfgang Geyer**, **Volker Stadler**, **Alexander Küller**, **Michael Grunze**, Angewandte Physikalische Chemie,

Universität Heidelberg, GERMANY; Thomas Weimann, Peter Hinze, Physikalisch-Technische Bundesanstalt, Braunschweig, GERMANY.

We present new results in the generation of chemical nanostructures on aromatic self-assembled monolayers. Using electron beams, biphenyl monolayers on gold and silicon are cross-linked on the nanometer scale while reducible terminal groups such as nitro or cyano are locally reduced to amino functionalities. Additional molecules can be coupled stepwise to the nanopatterns so that chemically defined nanostructures with lateral dimensions below 20 nm are generated. Alternatively, the patterns can be transferred into the substrates by wet chemical etching processes. We present XPS and IR data of the chemical transformations as well as AFM profiles of the modified surfaces.

SESSION H2: PLASMON PROCESSES ON THE NANOSCALE

Chairs: David P. Taylor and Thomas Orlando
Monday Afternoon, December 2, 2002
Room 309 (Hynes)

1:30 PM *H2.1

SMALL IS DIFFERENT; SOME INTERESTING PROPERTIES OF MATERIAL CONFINED IN TIME AND NANOMETER SPACE OF DIFFERENT SHAPES. Mostafa A. El-Sayed, Georgia Institute of Technology, Department of Chemistry and Biochemistry, Atlanta, GA.

The property of a material is characterized by a specific length scale for the motion of its electrons. This itself is determined by the forces acting on the electrons. For metals, the mean free path of the electron determines its conductivity. For semiconductor, the Bohr Radius (the electron-hole separation induced by giving the semiconductor the minimum amount of energy required to separate its electron and hole i.e. the band gap energy) is the characteristic length scale. These characteristic length scales are on the nanometer dimension. What happens if we physically reduce the size of a material to be comparable or smaller than its natural (God given) characteristic length scale? Naturally, its property will change, and equally important, becomes sensitive to its size or its shape. Thus each material can, in principle, has multitudes of new properties as we change its size or shape on the nanometer length scale. In my talk, I will present our results on the change in the properties of some semiconductor and metallic nanoparticles(1) upon changing their shape. The properties studied are, the optical and nonradiative properties, the femtosecond electron dynamics in semiconductor nanoparticles, and the ultrafast photothermal shape changes of gold nanorods to spheres.

(1) For reviews see: a) Mostafa A. El-Sayed "Some Interesting Properties of Metals Confined in Time and Nanometer Space of Different Shapes", Acc. Chem. Research, 34, (4), 257-264 (2001). b) Stephan Link and Mostafa A. El-Sayed, "Shape and size dependence of radiative, non-radiative and photothermal properties of gold nanocrystals", Int. Reviews in Physical Chemistry, 19 (3) 409-453 (2000).

2:00 PM *H2.2

TAILORING NANOPARTICLES WITH LASER LIGHT. Frank Träger, Universität Kassel, Kassel, GERMANY.

The physical and chemical properties of nanoparticles or, more generally speaking, nanostructures, i.e. systems of reduced dimensions, depend on their size and shape and usually differ considerably from those of the corresponding bulk material of macroscopic dimensions. Therefore, assembly of such aggregates of precisely controlled size and shape on substrate surfaces or in encapsulating matrices opens the door to fabricate tailor-made materials with novel optical, structural, chemical and other functional properties. Technical exploitation of nanoparticles, however, is intimately connected to the availability of advanced techniques to produce, manipulate and characterize them in such a way that the genuine identity of each single entity is preserved while precisely controlling the dimensions. This paper gives an overview of current techniques to generate metal nanoparticles of controlled dimensions and, in particular, monodisperse ensembles. Special emphasis is given to manipulation of supported nanoparticles through irradiation with continuously tunable laser light either after or during particle formation, methods that rely on excitation of surface plasmon polaritons in the particles and exploit the size and shape dependence of the resonance frequencies of this collective electron oscillation for selective manipulation [1,2]. They are applicable to a variety of metals, a very wide size range and cannot only be used for narrowing of broad size distributions and fabrication of almost monodisperse nanoparticles but even to control the particle shape independent of size. Examples of laser treatment of silver and gold nanoparticles will illustrate the enormous potential of these techniques. Finally, future developments, prospects and applications will be outlined.

2:30 PM *H2.3

SUBWAVELENGTH SCALE PHOTONIC STRUCTURES.

Harry A. Atwater, Stefan A. Maier, Pieter Kik, Andrea Martin, Thomas J. Watson Laboratory of Applied Physics, California Institute of Technology, Pasadena, CA.

The ultimate miniaturization of photonic devices towards densely integrated optical systems akin to their electronic counterparts will require structures that focus, direct, guide and switch electromagnetic (EM) energy below the diffraction limit of light. We are investigating the possibility of using structures consisting of ordered arrays of closely spaced coupled dipole oscillators, such as metal nanostructures, for this purpose. We have developed a device/circuit theory that predicts that energy transport in these arrays occurs via resonant near-field coupling between metal nanostructures that sets up coupled plasmon modes of the nanostructured arrays. This coupling leads to coherent propagation of energy along nanoparticle and nanorod arrays with group velocities of about 0.1c and energy can be guided around 90 degree corners and split via tee structures with high efficiency. We have confirmed our theoretical predictions in a macroscopic analogs operating in the microwave regime both via experiment, full field electrodynamic simulations and far field spectroscopy of nanostructure arrays. In order to verify the guiding properties at the nanoscale, we fabricated ordered arrays of closely spaced 30-50 nm gold and silver nanostructures in a variety of geometries such as straight lines, corners and tee structures using electron beam lithography on ITO coated glass substrates and assembly using atomic force microscope manipulation. We are currently working on the optical characterization of these structures using an illumination mode near field scanning optical microscope (NSOM) as a local excitation source at 514 nm close to the surface plasmon frequency of gold nanoparticles. If the guiding of electromagnetic energy at optical frequencies on the nanoscale proves to be of the same efficiency as it is in the macroscopic microwave analog, then ordered arrays of metal nanoparticles could become building blocks of nanoscale all-optical integrated circuits.

3:30 PM *H2.4

OPTICAL NANOLITHOGRAPHY USING EVANESCENT FIELDS.

Richard Blaikie, Maan Alkai, University of Canterbury, Department of Electrical and Computer Engineering, Christchurch, NEW ZEALAND.

Resolution limits for projection optical lithography are well known and well understood, but in the optical near field region these limits can be overcome. This offers the possibility of performing optical nanolithography without the need to use expensive, deep ultraviolet light sources [1]. We have been studying photolithography techniques that utilise exposure from evanescent fields close to metallic amplitude masks. Sub-diffraction-limited resolution has been achieved experimentally, and the theoretical resolution limits have been explored using vector electromagnetic near field simulations. Resolution down to 20nm using exposure wavelengths greater than 400nm is predicted [2]. In this talk the issues affecting the fundamental resolution photolithography using evanescent fields will be explored. It is found that the exposure wavelength is of secondary importance in this regime, and that the properties of the mask are much more significant. Scaling to smaller feature sizes requires better resolution and control during mask manufacture, rather than the conventional (and costly) approach of driving the exposure wavelength deeper and deeper into the ultraviolet. Near field interference effects will also be discussed, and a proposal for spatial frequency doubling using Evanescent Interferometric Lithography (EIL) will be described [3]. Finally, some recent results will be presented on the use of negative refraction and surface plasmons to improve further the resolution in the evanescent near field. 1. Alkai, et al., Appl. Phys. Lett. 75, 3560 (1999); Goodberlet, Appl. Phys. Lett. 76, 667 (2000). 2. McNab and Blaikie, Appl. Opt. 39, 20 (2000). 3. Blaikie and McNab, Appl. Opt. 40, 1692 (2001).

4:00 PM H2.5

PLASMON PRINTING - NANOSCALE PATTERN REPLICATION USING VISIBLE LIGHT. Andrea L. Martin, Pieter G. Kik, Stefan A. Maier, Harry A. Atwater, California Institute of Technology, Thomas J. Watson Laboratory of Applied Physics, Pasadena, CA.

We have recently proposed a new approach to optical lithography that could be used to print patterns with feature sizes below 50 nm using conventional photoresists. This work exploits the intensity enhancement at the plasmon resonance of metal nanoparticles i.e., the collective electron oscillation (surface plasmon mode) in an optical field. Resonant excitation of metal nanoparticles produces a strongly enhanced dipole field, and a thin resist layer can be locally exposed in the resonantly enhanced near field region. Using Finite Difference Time Domain (FDTD) simulations we show that broad beam illumination produces an enhanced local intensity that varies in position depending on the incident angle of the beam. From the

FDTD simulations the enhanced exposure area for a 40nm Ag sphere using p-polarized 439nm light directly incident on the sample is 30-80 nm in diameter (0.05 l) and extending to depths of 12-45 nm in the resist. The optimum illumination wavelength coincides with the high sensitivity region of standard g-line photoresist. We also explore the importance of the medium above and below the resist layer and the angle of incidence. Printing experiments using 40nm diameter silver colloid deposited directly onto the 55-75 nm thick g-line resist layers on PDMS and using contact lithography with masks containing 30nm diameter silver structures prepared with lift-off technique will be presented. The samples were exposed at various times using ~400nm light and subsequently developed. Atomic Force Microscopy and UV NSOM on these samples reveals nanoscale depressions in exposed resist layers, providing evidence for plasmon-enhanced resist exposure. We will discuss potential applications as well as some limitations of the technique. [1] P.G. Kik, S.A. Maier, and H.A. Atwater, "Plasmon Printing - a new approach to near field lithography", Nanopatterning - from Ultralarge-Scale Integration to Biotechnology (Mat. Res. Soc. Proc., Boston 2001).

4:15 PM H2.6

THE CONSTRUCTION OF SPHERICAL ASSEMBLIES BY GOLD NANOPARTICLES MEDIATED WITH MULTI-DENTATE THIOETHER LIGANDS. Mathew M. Maye, Li Han, Stephanie Lim, Chuan-Jian Zhong, Department of Chemistry, State University of New York at Binghamton, Binghamton, NY; Daniel Rabinovich, Department of Chemistry, The University of North Carolina at Charlotte, Charlotte, NC.

The synthesis and processing of nanoparticles consisting of metallic nanocrystalline cores and organic monolayer shells promise interesting technological applications in sensors, catalysis, drug delivery, microelectronics and medical diagnostics. However, the ability to assemble them with controllable dimensions and spatial properties is still very limited. This presentation describes novel findings of the assembly of gold nanoparticles via multidentate organosulfur molecules. Tetraoctylammonium-capped gold nanoparticles were utilized as building blocks, and thioethers with different binding sites were used as mediators. The reactivity and kinetics were monitored using uv-visible spectrophotometry, which provided information about the correlation of the surface plasmon resonance band with the concentration and the structure of the molecular mediator. The interfacial replacement of the tetraoctylammonium by the thioether ligand was assessed by FTIR spectroscopic characterization. The morphological evolution from individual nanoparticle to spherical assembly with diameters of 80 ~ 200 nm was demonstrated by TEM visualization. The "soft" nature of the spherical assembly on different substrates was probed by AFM imaging study. The results reveal an intriguing interaction-induced morphological change. Implications of the findings to interfacial manipulation of the nanostructures and potential applications will also be discussed.

4:30 PM H2.7

DIRECTED SELF-ASSEMBLY OF ORDERED METAL NANOCRYSTAL ARRAYS USING A FOCUSED ION BEAM MICROSCOPE (FIB). M.D. McMahon, A.B. Hmelo, R. Lopez, R.F. Haglund Jr., L.C. Feldman, Dept of Physics and Astronomy, Vanderbilt University, Nashville, TN; R.A. Weller, Dept of Electrical Engineering and Computer Science, Vanderbilt University, Nashville, TN; R.H. Magruder III, Dept of Electrical Engineering and Computer Science, Vanderbilt University, Nashville, TN, and Dept of Physics, Belmont University, Nashville, TN.

Metal nanocrystals are strongly confined electronic systems with a band structure drastically altered by the small size of the system and the reduced population of conduction-band electrons. Their optical response is extremely sensitive to the size, size distribution and spatial arrangement of individual nanocrystals. Ordered arrays of metal nanoparticles have potential applications as elements of nonlinear or near-field optical circuits, as sensitizers for fluorescence emitters and photodetectors, and as anchor points for arrays of biological molecules. This effort is focused on the fabrication of ordered metallic nanocrystal arrays for optical investigations. Our approach is to promote the formation of metal nanocrystals on a spatially arranged lattice of holes prepared by focused ion beam (FIB) processing of a substrate. The holes were formed by FIB drilling in a silicon substrate with a 25 nm surface oxide. Two processes have been explored: 1) Fabrication of ordered arrays of gold nanocrystals on FIB-processed substrates using electroless deposition; and 2) Fabrication of ordered arrays of silver nanocrystals with diameters 40-60 nm separated by 180 nm center-to-center, using pulsed-laser deposition (PLD) to deposit silver on the substrate. The metal nanocrystal arrays are characterized using AFM as well as SEM and energy dispersive x-ray (EDX) analysis. EDX analysis demonstrates that Ag preferentially clusters at sites that have been irradiated by the ion beam. These results suggest that the FIB-PLD combination can be used to create ordered arrays of Ag nanocrystals with

diameters of 10 nm or less. This research has been supported by the U.S. Department of Energy under grant DE-FG02-01ER45916.

4:45 PM H2.8

NEW PROCESSING TECHNIQUES FOR THE CREATION OF MICRO-OPTO-ELECTRO-MECHANICAL MACHINES AND PHOTONIC DEVICE IMBEDDED IN GLASS. Meg Abraham, Oxford University, Dept of Materials, Oxford, UNITED KINGDOM.

Photo-writable glass is a commercially available material that can be patterned using a standard UV photon exposure and bake process. It has been developed to allow for the exposure of metal ions in the glassy matrix that can form nano-crystalline nucleation sites and eventually small SiO₂ or metal crystals when annealed at higher temperatures. To date the use of photo-writable glasses in the area of MEMS research has concentrated on the improvement of the exposure and etch techniques for the purpose of making small high-aspect ratio mechanical devices in this medium. This approach has been used to make gross imbedded features in the glass. We are currently developing new ways of extending the functional use of this material to the areas of MOEMS and photonics by incorporating advanced laser and ion based techniques. The immediate aim is to further reduce the scale of imbedded structures in the glass to form wave-guides of various types. The techniques being investigated include: the extension of the glass type to materials which form metal needles (as opposed to SiO₂ crystals) that can be used in plasmon applications, the use of an ion beam to expose the glass and create very small imbedded nucleation sites for crystal growth, and the use of laser direct write for both the exposure and the etching of the glass. We will show the potential advantages of each of these areas of research for creating rigid waveguides in transparent medium.

SESSION H3: NANOFABRICATION VIA NONLITHOGRAPHIC TECHNIQUES

Chairs: Thomas Orlando and Koji Ikuta
Tuesday Morning, December 3, 2002
Room 309 (Hynes)

8:30 AM H3.1

SHAPE VARIATIONS AND CONTROL IN SELF-ASSEMBLED METAL NANOCCLUSERS. Rina Tannenbaum, Georgia Institute of Technology, School of Materials Science and Engineering, Atlanta, GA.

The use of polymers as stabilizing agents for the controlled synthesis of metal nanoclusters can be extended also to the manipulation of cluster shape. The preferential adsorption of polymers to distinct crystallographic faces of the growing metallic fragments, causes a distortion of the cluster shape, since the growth directions become differently hindered by the polymer. The result is a high degree of anisotropy in the cluster shape. Various iron-polymer systems are studied in order to determine the precise parameters which govern such preferential adsorption. Systems in which the same polymer has been used but the reaction conditions were different, exhibited different particulate shape. For example, in the presence of poly(vinylidene difluoride) (PVF₂), the thermal treatment of a metal precursor-polymer solution that is concurrent with solvent removal and polymer film formation ("hot" method), gives rise to nanopillars. On the other hand, the thermal treatment of a metal precursor-polymer solution that is performed after solvent evaporation at room temperature (cold method), gives rise to nanospheres. In the former case, the solvent is present in the initial stages of the reaction, allowing a higher degree of mobility of the growing nanoclusters and the polymer chains, while in the latter case, the metal precursors are immobilized in the polymer film. Additional examples include the formation of Fe nanorods in the presence of poly(methyl methacrylate) (PMMA), and the formation of nanostrings in the presence of poly(carbonate) (PC). As an important step in understanding the underlying molecular mechanisms responsible for the shape selectivity of metal nanoparticles in the presence of various polymers, we will attempt to relate the particle shape variation to the strength of the metal-polymer interaction and the effectiveness of the capping process by the adsorbed polymer layer.

9:00 AM H3.2

SELF-ASSEMBLED HIERARCHICAL-STRUCTURES OF EMULSIONS AND FINE PARTICLES. Sachiko I. Matsushita, RIKEN Frontier Research System, Dissipative-Hierarchy Structures Lab, Saitama, JAPAN; Nobuhito Kurono, Masatsugu Shimomura, Hokkaido Univ, Research Institute for Electronic Science, Hokkaido, JAPAN.

Various production methods such as conventional lithography, soft lithography, self-assembly, are used to obtain nanoscale to microscale architectures, which are considered extremely important from the

point of view as photonic crystals, electron emitters, high-density optical storage media, catalytic systems, and so on. Among them, since Prigogine won the novel prize in 1977, dissipative process is well known that it is potentially of great scientific and technological interest because the process is simple, self-assembly, inexpensive system to prepare wide-range architecture, from nanometer to micrometer size. Especially, one of the important points of dissipative process is capability to make hierarchy structures that will birth diversity and complexity, as every creature does. Among many dynamic processes such as dissipative structures, we attracted honeycomb-like structures. This honeycomb-like structure can be formed in a volatilized process of polymer suspensions by exposure in humidity air, and the final structure has hexagonally hole-packed air-spheres (0.2 - 10 μm diameter) like a comb of honeybees. Possible applications of such honeycomb structures itself include membranes for separation, microreactors, biointerfaces, catalysts, and microstructured electrode surfaces, however, in this presentation, a new application as a self-assembly system to prepare hierarchical structures would be reported. Honeycomb structures are basically made from water/oil emulsions covered with surface-active agents. On the basis of this knowledge, this work tries to put some materials into those water/oil emulsions, and form those materials into honeycomb structures. As the results, a periodic hierarchically array composed of microporous polymer micelles and submicro fine polystyrene particles, named "Honey-Beads", can be easily prepared using the formation of original honeycomb structure. This honey-beads morphology is drastically changed with the experimental condition: The size of a larger hierarchy can be controlled to 1 to 3 μm , and the one of a smaller hierarchy can be controlled to 0.25 to 1 μm .

9:15 AM H3.3

VAPOR PHASE DEPOSITED NANOCOMPOSITES OF POLYMER CONTAINING THREE DIMENSIONALLY DISPERSED METAL CLUSTERS. A. Biswas, J. Kanzow, J. Kruse, V. Zaporotchenko, T. Strunskus[†] and F. Faupel, Lehrstuhl für Materialverbunde,

Technische Fakultät der CAU, Kiel, GERMANY. [†]Lehrstuhl für Physikalische Chemie I, Ruhr-Universität, Bochum, GERMANY.

Nanocomposites two component materials consisting of finely dispersed mixtures of metal clusters and polymer are of interest both from the fundamental and technological aspects in terms of several new nanomaterial properties. The microstructure and many physical properties of such composites depend on the method of preparation. A completely solvent free and easy technique of vapor phase thermal evaporation is employed to prepare nanocomposites of polymer containing metal clusters. Nanocomposites of three dimensionally dispersed different metallic nanoclusters (Ni, Au, Cu) in various polymer matrices (Teflon AF, PI) are fabricated by following co-evaporation to tandem deposition in the form of many sequential evaporation of the two components. Production of homogeneously distributed nanoclusters with narrow size distribution embedded in polymer matrices is accomplished. Tandem evaporation method particularly demonstrates that the cluster size and distribution can be controlled independently with cluster volume filling. Some of the optical and magnetic properties of the prepared composites are also discussed.

9:30 AM *H3.4

THE FORMATION, CHARACTERIZATION, AND INTEGRATION OF NANOSTRUCTURES: Ag AND Si. John H. Weaver, University of Illinois, Department of Materials Science and Engineering, Urbana, IL.

In the area of nanostructures, the goal is to produce structures of arbitrary material on a substrate of arbitrary material, with size selection and patterning so that new science can be learned and new devices can be fabricated. There are many ways to approach this synthesis, and all have their limitations. In our laboratory, we have developed a way to produce clusters or nanostructures of a wide range of materials and to deliver them to atomically clean surfaces (of any type) where their interactions can be investigated. The process involves vapor deposition onto inert solid surfaces of Xe where nucleation and growth occurs at 50 K. Subsequent desorption of the Xe delivers the clusters in the ultimate of "soft landing". This talk will emphasize Ag and Cu clusters delivered to surfaces derived from Si(111)-7x7 or from Ag(111). Scanning tunneling microscopy makes it possible to explore issues related to wetting, atomic rearrangement, interface bonding and adhesion, and manipulation. STM results show that these nanocrystals range in size from 100 to 600,000 atoms, depending on growth parameters, and we will emphasize their novel properties. For example, silver nano-crystals on Si(111) could be pushed by mechanical contact with the tip, and they left behind a Ag track due to site-selective Ag atom transfer to the Si surface. Copper nanocrystals could not be moved but they could be sheared by tip contact. Ag clusters delivered to ideal Ag(111) wetted the surface and produced hexagonal multilayer epitaxial islands that decayed via step-step contact while maintaining a constant mean terrace width of ~ 11 Å. Equivalent decay was not observed for Ag on strained Ag

surfaces. Finally, the STM tip can also be used to produce patterns and cause clusters to merge. Extensions of this growth procedure will be discussed, along with possible ways to achieve patterning.

10:30 AM *H3.5

WIND-DRIVEN WAVES AT A MOLECULAR SEASHORE. C. Mathew Mate, IBM Almaden Research Center, San Jose, CA.

We have all noticed the intricate wave patterns that wind generates on the surfaces of lakes and oceans. On these macroscopic liquid surfaces, the driving force for wave formation is wind shear, while the forces of gravity, surface tension, and viscosity work to smooth these surfaces. In this talk, I show how wind shear can generate and manipulate wave patterns on the surfaces of molecularly thin liquid films. For these ultra-thin films, molecular forces dominate over the forces of gravity and surface tension and concept of viscosity breaks down, leading to wide variety of novel wave patterns. The most exciting results are for films susceptible to dewetting, as the repulsive interactions between the liquid molecules and the solid substrate help to amplify surface wave patterns. Three types of wind driven wave patterns are observed for dewetted films: (1) dewetting patterns that are locked to the underlying substrate and liquid molecules flow through the dewetted nanostructures when blown across the surface; (2) dewetting patterns that travel with the molecules across the surface; and (3) initially smooth molecular films that can be roughened by slight breeze over the surface. I will discuss the implications of these results for lithography of nanometer thick films and the potential for using wind driven dewetting for nanostructuring surfaces.

11:00 AM *H3.6

RESOLUTION, FIDELITY, AND REGISTRATION OF DIRECTLY PRINTED PATTERNS OF MICROELECTRONIC MATERIALS.

Sigurd Wagner, Scott M. Miller, Anton A. Darhuber, Samir Succar, and Sandra M. Troian, Depts of Electrical and of Chemical Engineering, Princeton University, Princeton, NJ.

The direct printing of patterned active electronic materials has been attracting considerable attention recently, because it could reduce the cost of electronic circuits and MEMS well below of those fabricated by the conventional deposition, modification and patterning of device layers. This cost reduction may derive from the reduction of process steps, massively parallel printing of large areas, or roll-to-roll manufacture. At present the dominant application of direct printing is making printed-wire boards, where passive components like capacitors are printed in addition to interconnects. It is likely that direct printing will extend up to large area electronics as well as down to micro and nanostructures, perhaps even covering the entire range of scale in the form of large-area nanoelectronics. Printing a device layer needs a printing technique, an "ink" and a process that converts the ink to the electronic material. Overlay registration becomes important when complete devices must be printed. A large range of printing techniques is available; it covers impact and non-impact printing, with impact printing including additive and displacement techniques. To date few inks and process have been developed specifically for the printing of active electronics. Therefore demonstrations of printing have been dominated by the inks that are available rather than by the devices that are desired. This situation explains the preponderance of printed etch masks instead of device layers, which are more demanding. The principal issues associated with any printing technique are the resolution of the printed device layer and the fidelity of the printed pattern to the desired design. No new technique has been demonstrated for overlay alignment. We will categorize the issues associated with the direct printing of electron devices, and focus our discussion on pattern production and pattern fidelity.

11:30 AM H3.7

DIRECT IMPRINTING OF A LASER FEEDBACK STRUCTURE INTO A LIQUID-CRYSTALLINE ELECTROACTIVE

CONJUGATED POLYMER. Erik Moderegger, Guenther Leising, AT&S AG, Science & Technology Scientific, Leoben, AUSTRIA; Emil J.W. List, Christian Doppler Laboratory for Advanced Functional Materials, Graz University of Technology & Joanneum Research, Graz, AUSTRIA; Roland Guentner, Ullrich Scherf, University of Potsdam, Institute for Physical and Theoretical Chemistry, Golm, GERMANY.

The realization of an polymeric injection laser diode is an important aim in organic electronics. A step towards this goal lies in the understanding and fabrication of feedback structures for lasers. Such a feedback structures may either be fabricated in the substrate or directly in the active polymer layer. Soft Lithography has proven itself as a useful tool to pattern a wide variety of materials. Typically one uses elastomeric molds (stamps) to pattern materials and structures with dimensions as low as 30 nm can be achieved. We present a direct imprinting process based on soft lithography to fabricate a laser feedback structure directly onto a liquid-crystalline type electro active conjugated polymer. The utilized polymer allows for a low

temperature imprinting process due to its low glass transition temperature. We will report on the application of this approach to produce optical feedback structures for optically pumped laser arrays.

11:45 AM H3.8

NANOSCALE SCIENCE & TECHNOLOGY - A GATEWAY TO NEW PRODUCTS, PROCESSES AND PROPERTIES IN THE CHEMICAL INDUSTRY. Raymond Oliver, David Sutton, Derek Graham, ICI Strategic Technology Group, Redcar, UNITED KINGDOM.

The Chemical and Process Industries (CPI) has witnessed massive change over the last decade. Much of the Oil and Petrochemicals industry production has shifted irrevocably to the Middle and Far East and has been replaced by biochemical and specialty materials market opportunities. Waiting in the wings is the huge potential offered by "small technology" concerning nanoscale and nanostructured materials generation. In this talk I will try to give a view of some of these opportunities from the point of view of a specialty materials and consumer products business and in particular how Chemical Engineering Principles still apply even although the process/product technologies are closer to those developed for semiconductor and electro ceramics industry sectors. It is also a fact that most fine materials and structured materials in the chemical industry are synthesised and assembled from a fluid phase which can be a simple single component system or may be complex consisting of two or more phases in the presence of surface active molecules for example. The ability to process such materials without losing valuable structure and organisation within the material is a key element of providing useful Nanoscale materials. The trend over the next few years will then be to move towards Molecular Manufacturing principles through scale-down, replication and so called "bottom-up" product synthesis and assembly with an increasing emphasis on effect and functionality while still retaining efficiency and availability. In this context "granular materials" has to be viewed in hierarchical terms, where the relevant length scale may move from approximately 100microns for bulk storage and flow to 1micron for redispersible aggregated primary particles to 1-10 nm for "quantum dot" type nanoclusters which exhibit spectacular changes in luminescence for example. I will illustrate the above with examples of nanoscale synthesis and assembly processing technologies which deliver extreme effects and functionality.

SESSION H4: FABRICATION AND PROPERTIES OF 2D-ORDERED NANOSTRUCTURES

Chairs: Koji Ikuta and Lhadi Merhari
Tuesday Afternoon, December 3, 2002
Room 309 (Hynes)

1:30 PM *H4.1

TWO-DIMENSIONAL ORDERED NANO PORE ARRAYS: FABRICATION AND FILLING WITH MATERIALS. Ulrich Goesele, Kornelius Nielsch, Frank Mueller, Sven Matthias, Manfred Reiche, Ralf Wehrspohn, Jinsub Choi, Max Planck Institute of Microstructure Physics, Halle, GERMANY.

We have investigated two-dimensional ordered pore arrays and their filling with materials such as various metals based on two different material systems. One material system involves pore arrays in silicon, the other one pore arrays in aluminum oxide fabricated by anodic oxidation of silicon. In the case of silicon the location of the pores has to be predefined lithographically. The pore diameter can be varied during the etching process. Subsequent filling with a metal leads to metal rods with varying diameter. The diameter variation may be used to encode information in an optically readable way. In the case of anodic oxidation the ordering of the pores is based on a self-limited process which does not allow long range order. Long range order may be obtained by a combination of nano-imprint and self-ordering. Filling of the pores with ferromagnetic materials allows to fabricate ordered ensembles of ferromagnetic nano-wires which might be of interest for future high-density magnetic storage concepts. Further examples of filling of pore arrays will be given.

2:00 PM *H4.2

3-D NANOSTRUCTURE FABRICATION BY NANOIMPRINT LITHOGRAPHY & LITHOGRAPHICALLY INDUCED SELF-ASSEMBLY Paru Deshpande, Zhaoqing Yu, Wei Wu, Mingtao Li, Bo Cui, Xinya Lei and Stephen Y. Chou, NanoStructure Laboratory, Department of Electrical Engineering, Princeton University, Princeton, NJ.

As semiconductor devices continue to shrink, low-cost, large area, 3D nanoscale patterning is becoming increasingly significant. Such 3D nano-patterning is also needed in areas such as nano-optics, nanobiology and MEMS/NEMS just to name a few. In this talk, we present two innovative approaches to large area nanofabrication that

can be extended to three-dimensional structures. The first, nanoimprint lithography (NIL), is a low cost, high throughput nano-patterning process in which a mold is used to physically deform a polymer resist (1). Sub-10 nm feature sizes and uniformity over large areas have both been demonstrated. Using a 3D mold, 3D patterns can also be created. The second is lithographically induced self-assembly (LISA), a process in which a mask held above a thin polymer film is used to induce periodic pillar arrays in the polymer (2). The pillars bridge the gap between the substrate and mask. Furthermore, the pillars can be aligned to patterns in the mask allowing for precise control of the position and crystal structure of the pillar arrays. Such structures can be used as interconnects for 3D architectures or as features on top of pre-existing patterns.

1. S.Y. Chou, P.R. Krauss and P.J. Renstrom, *Science* **272**, 85-87 (1996).

2. S.Y. Chou and L. Zhuang, *Journal of Vacuum Science & Technology B* **17**, 3197-3202 (1999).

2:30 PM *H4.3

OPTOELECTRONIC NANOSTRUCTURES. Gernot S. Pomrenke, Air Force Office of Scientific Research, Arlington, VA.

Nanotechnology and nanoengineering as applied to optoelectronics offer opportunities and challenges for next generation devices. The convergence of nanotechnology, material processing, tools, and applications is driving the realization of integrated photonics and the all photonics chip. Part of this approach is photonic crystals. Building these crystals requires creating periodic structures from dielectric materials that repeat themselves exactly and at regular intervals. If the matrix is made precisely the resulting structure may have a photonic bandgap, a range of forbidden frequencies within which a particular wavelength may be blocked, and the electromagnetic radiation is reflected. Photonic bandgap structures and the associated nanofabrication allows photonics to advance optoelectronic miniaturization, light localization, and highly integrated optical devices and components. Lithographic techniques like focused ion beam, e-beam or extreme UV lithography play part in this miniaturization. However, these techniques have their limitations in terms of materials that can be patterned and the associated capital investment is high. Alternative techniques are needed based on self-assembly of inorganic and organic particles into regular nanostructures, soft lithography, nanopores, and protein and biological scaffolds. Example alternatives could be block copolymers that can be designed to mimic biological membranes, and diatoms with their intricately patterned wall that consists of amorphous silica. Understanding the molecular mechanisms that control these alternative types of nanofabrication will be a challenge.

3:30 PM H4.4

SELF-ASSEMBLY OF NANOSHEETS USING MAGNETIC FIELD. Jean-Christophe P. Gabriel¹, Franck Camerel, Patrick Batail, Sciences Moléculaires aux Interfaces, CNRS, Nantes, FRANCE; Bruno J. Lemaire, Patrick Davidson, Lab Physique des Solides, CNRS, Orsay Univ, FRANCE; Hervé Desvaux, Service de Chimie Moléculaire, CEA, Saclay, Gif-sur-Yvette, FRANCE; ¹Present address: Nanomix Inc., Emeryville, CA.

We will present the first example of a lamellar phase comprised of inorganic solid-like nanosheets (i.e. in which all atoms involved in the sheet are covalently bonded) dispersed in water. The spacing between these nanosheet can be tuned from 1.5 to 225 nm. Moreover, highly oriented bulk samples can be obtained by mechanical or magnetic alignment. This property was used to measure residual dipolar couplings for the structure determination of biomolecules by liquid-state NMR.

3:45 PM H4.5

GELATION OF A SYNTHETIC, β -SHEET-DERIVED PEPTIDE. Nathan Lockwood, Univ of Minnesota, Dept of Chemical Engineering and Materials Science; Robert van Tankeren, Kevin Mayo, Univ of Minnesota, Dept of Biochemistry, Minneapolis, MN.

We observed gelation of a 23-residue peptide derived from the β -sheet domain of platelet factor-4 (PF4₂₄₋₄₆). Optical and electron microscopy revealed gels composed of heterogeneous mixtures of 50 to 200 μ m spherical aggregates in a less-dense gel matrix. Infrared and circular dichroism spectroscopies showed that gelation involved the conversion of PF4₂₄₋₄₆ from an unstructured, random coil state to an extended β -sheet conformation. We used aggregation-induced NMR peak intensity decay to show that temperature, pH, and ionic strength influenced PF4₂₄₋₄₆ gelation rates. Under identical solution conditions, gel formation took days at $T \leq 20^\circ\text{C}$, but only 30 minutes at $T \geq 50^\circ\text{C}$. Gelation was most rapid at pH values near the pKa of His35, the central residue of the peptide. Increases in solution ionic strength reduced the critical gelation concentration of PF4₂₄₋₄₆. The results of our study share characteristics of self-assembling peptides reported by other groups. Based on our results, we pose a hypothetical

model of PF₄-46 gelation in which the development of parallel or antiparallel β -sheet character leads to extensive self-assembly via intermolecular hydrogen bonding, followed by hydrophobic associations of the resultant β -sheets into extended networks. Intermolecular electrostatic repulsions between peptide sidechains and N-termini moderate the rate and extent of self-assembly.

4:00 PM H4.6

SYNTHESIS AND CHARACTERIZATION OF METAL NANO-PARTICLES IN AMORPHOUS CARBON FILMS. I. Gerhards, H. Hofsäuss, and C. Ronning, II. Physikalisches Institut; H. Gibhardt, Institut für Physikalische Chemie; M. Seibt, IV. Physikalisches Institut, Universität Göttingen, Göttingen, GERMANY.

Metallic particles in the size of a few nanometers embedded in a dielectric matrix material offer a wide range of qualities, as for example nonlinear optical behavior, enhanced field emission properties, or the potential use for high density recording media. This motivated our study on the formation of metal nano-particles in diamond-like amorphous carbon (a-C). The structural properties of metal containing amorphous carbon thin films (a-C:Me, Me = Cu, Ag, and Fe) synthesized by mass selected ion beam deposition (MSIBD) have been characterized using X-ray photoelectron spectroscopy (XPS), Auger electron spectroscopy (AES), electron energy loss spectroscopy (EELS), Rutherford backscattering (RBS), Raman spectroscopy, X-ray diffraction (XRD), and transmission electron microscopy (TEM). Films were grown with varying metal to carbon ion ratios at room temperature on silicon substrates by co-deposition of low energy carbon and metal ions. The carbon matrix proves to be diamond-like with a high sp³-bonding content at low metal concentrations and becomes more graphitic with increasing metal content. Copper forms nano-particles within the matrix due to the vanishing solubility in carbon. The sizes of the embedded Cu clusters are in the order of nanometers and vary with the Cu concentration. These and other dependencies will be presented together with model assumptions on the formation mechanism of the clusters upon ion beam impact.

4:15 PM H4.7

A BOTTOM-UP APPROACH TO POLYMER/CARBON NANOTUBE FILMS. Jason H. Rouse^a, Peter T. Lellehei^b, Emilie J. Siocchi^b; ICASE^a; Advanced Materials and Processing Branch^b; NASA-Langley Research Center, Hampton, VA.

The use of molecular interactions to assemble polymer/single walled carbon nanotube (SWNT) films will be discussed. Using oxidized groups present on carbon nanotubes, films have been formed via the repetitive electrostatic adsorption of carbon nanotubes onto surfaces treated with a positively charged polymer. Films prepared by this sequential adsorption method displayed linear growth characteristics as monitored by absorption spectrophotometry. Both probe and electron microscopy of these films revealed that films could be prepared which contain a very-high concentration of SWNTs. The use of a bottom-up approach to assemble polymer/SWNT composite films allows an unprecedented level of control over film structure. We will demonstrate that by varying the adsorption conditions, one can tailor the amount, orientation, and vertical placement of the SWNTs within the film.

4:30 PM H4.8

SELF-ORGANIZED ZnO NANOSIZE ISLANDS WITH LOW-DIMENSIONAL CHARACTERISTICS ON SiO₂/Si SUBSTRATES BY METALORGANIC CHEMICAL VAPOR DEPOSITION. Sang-Woo Kim, Shigeo Fujita, Kyoto Univ, Dept of Electronic Science and Engineering, Kyoto, JAPAN; Shizuo Fujita, Kyoto Univ, International Innovation Center, Kyoto, JAPAN.

ZnO is a semiconducting material with a wide band gap of 3.3 eV at room temperature. Due to its remarkable excitonic properties based on the large excitonic binding energy (60 meV), significant exciton effects promising for achieving large oscillator strength, nonlinear optical properties, or multiexciton interaction may be expected in low-dimensional ZnO nanostructures. In this paper, we report the successful growth of ZnO nanosize islands with low-dimensional characteristics, which may lead to the enhanced exciton confinement, on SiO₂/Si substrates by metalorganic chemical vapor deposition by introducing either N₂O or NO₂ gas as an oxygen source and diethylzinc as a zinc source on thermally grown SiO₂ layers on Si (111) as a function of the growth time, the substrate temperature, and the source flow rate. Investigation by atomic force microscopy showed that the density and size of the ZnO islands were changed by the growth conditions. Reactive NO₂ rather than N₂O as an oxygen source was found to be a key in order to obtain uniform ZnO nanosize islands with narrower size distribution and higher density. At the present stage, the height distribution was varied from 3 to 14 nm and the density in the order of 10¹⁰ cm⁻² could be obtained. More recent

study is effectively going on to decrease the size and increase the density. In macroscopic photoluminescence measurements at 10 K using a 325 nm He-Cd laser, we observed the broad peak with a band tail up to about 3.55 eV located at the higher energy with respect to band edge emission of bulk ZnO with the free exciton emission located at about 3.38 eV. This result indicates that these ZnO nanosize islands have low-dimensional quantum effect characteristics. Detailed optical characterizations are still in progress.

4:45 PM H4.9

MORPHOLOGY EVOLUTION OF PYRAMID-LIKE NANOSTRUCTURES ON COBALT THIN FILMS DURING DEPOSITION BY SPUTTERING. Shih-Wei Chen, Jin-Ruey Wen, Chuan-Pu Liu, Department of Materials Science and Engineering, National Cheng-Kung University, Tainan, TAIWAN; Jiun-Nan Chen, Department of Electrical Engineering, Fortune Institute of Technology, Kaohsiung, TAIWAN.

The cobalt thin films are grown by D.C. magnetron sputtering as a function of the target-to-substrate distance, bias and power. The electrical properties, crystal structure and morphology of the thin films are characterized by 4-point probe, x-ray diffraction, scanning electron microscopy, transmission electron microscopy and atomic force microscopy. It is found that the cobalt crystal structure can be varied from HCP to FCC by varying the target-to-substrate distance from 6 to 10 cm. The resistivity, roughness and the preferred orientation of the thin films are greatly affected by the substrate bias and power. The lowest resistivity of Co films is 9.8 $\mu\Omega$ -cm when deposited at the target-to-substrate distance of 6cm, the applied power of 50W and substrate bias of -75 volts. In addition, pyramid-like nanostructures with sharp tips are formed on the surface of the thin films when negative bias is applied. The faceted planes on the nanostructures depend on the resulting Co crystal structure while the size and density are determined by the growth parameters. The evolution of the surface nanostructures are systematically examined as a function of substrate bias and thin film thickness. The formation mechanism of the surface nanostructures is discussed in the paper.

SESSION H5: FABRICATION AND PROPERTIES OF NANOWIRES, NANORODS AND NANOTUBES

Chairs: Koji Ikuta and Thomas Orlando
Wednesday Morning, December 4, 2002
Room 309 (Hynes)

8:30 AM *H5.1

SELF-ASSEMBLY OF MULTIDIMENSIONAL NANOROD STRUCTURES ON SURFACES. Sarah K. St. Angelo, Benjamin R. Martin, Thomas J. Larrabee, Thomas E. Mallouk, The Pennsylvania State University, Department of Chemistry, State College, PA.

We have studied a variety of surface-rod and rod-rod interactions using electrochemically grown nanorods (30-300 nm in diameter and 1-6 microns in length). These studies have provided us with strategies to attain two-dimensional and three-dimensional assemblies of nanowires. Typically, Au nanorods are derivatized with SAM forming molecules to define their surface chemistry and control their interactions. We have found that controlling the dimensions of the rods and their surface chemistry result in the formation of ordered phases resembling nematic and smectic liquid crystalline phases. Raft-like structures may be obtained by employing lithographically patterned substrates. Microcontact printing has been used to pattern surfaces with a variety of SAM forming molecules whose domains are commensurate with the rod dimensions. This spatially resolved surface chemistry allows us to assemble structures on relatively flat surfaces. We have developed a color-coding technique that aids in the visualization of structures as they are forming and provides us with a simple means to quantify surface diffusion and phase behavior of rods in these systems.

9:00 AM *H5.2

NANOWIRES AND NANOSPRINGS: UNEXPECTED CATALYST MEDIATED GROWTH PHENOMENA. David N. McIlroy, D. Zhang, A. Alkhateeb, H. Han, University of Idaho, Dept. of Physics, Moscow, ID; M. Grant Norton, Washington State University, School of Mech. and Mat. Eng., Pullman, WA.

The role of the metallic catalyst in the synthesis process of microwhiskers and nanowires has been well understood since the mid-1960s. Specifically, the metallic catalyst, when in the liquid phase, facilitates the absorption of material from the vapor phase. In turn, the absorbed material is transported through the catalysts to a solid interface where it is used to build the ensuing nanowire. This mechanism is known as the Vapor-Liquid-Solid (VLS) mechanism of filament growth. Only recently has the effects of the catalyst dynamics on nanowire geometry been realized. Under the appropriate conditions helical growth of nanowires, or nanosprings, can be

achieved. The prerequisites for nanospring formation are as follows: (1) The composition of the nanowire forming the nanospring must be amorphous, (2) the catalyst must have a spherical geometry, and (3) the catalyst diameter must exceed that of the nanowire forming the nanospring. To date, boron carbide nanosprings have been realized, however, the theoretical model of nanospring formation we have developed indicates that it is possible to synthesize nanosprings from a wide variety of semiconductor and ceramic materials. The catalyst also plays a critical role towards determining the composition of the nanowires or nanosprings. Specifically, by achieving the appropriate balance between precursor partial pressure, total pressure, substrate material and the solubility of elements within the catalyst, the elemental composition of the nanowires can be controlled. A detailed discussion on the feasibility of nanowire heterostructures based on composition modulation will be presented.

9:30 AM H5.3

CARBON NANOTUBE-CONDUCTING POLYMER NANOCOMPOSITES: STRUCTURE AND ELECTROCHEMICAL PROPERTIES. Mark Hughes, George Z. Chen, Milo S.P. Shaffer, Derek J. Fray, Alan H. Windle, University of Cambridge, Dept of Materials Science and Metallurgy, Cambridge, UNITED KINGDOM.

The electrochemical growth of carbon nanotube-conducting polymer composites offers the ability to produce three-dimensional nanostructured materials that combine the redox charge storage mechanism of conducting polymers with the high surface area and conductivity of carbon nanotubes. This desirable merging of properties presents new opportunities to produce superior materials for applications such as supercapacitors, sensors and actuators. The work described here relates to electrochemically grown composite films of multiwalled carbon nanotubes and conducting polymers such as polypyrrole and poly(3-methylthiophene). By manipulating such factors as the alignment, concentration, surface treatment, type and dispersion of nanotubes in these composites, it was found that the nanoporous composite structure and its electrochemical behavior could be closely controlled and customized. Interestingly, when negatively charged functional groups were attached to the nanotube surface using an acid-treatment process, the nanotubes were able to meet the dopant requirements of the conducting polymer during film growth, allowing excellent interaction between the nanotubes and conducting polymer. Using the factors described above, it was possible to minimize ionic diffusion distances within the nanoporous composite films, in addition to reducing their electrical and ionic resistance. Consequently, electrochemical capacitances in excess of 2.0 F/cm² were obtained for the composite films with rates of response that were more than an order of magnitude higher than those of similarly prepared pure conducting polymer films. These exceptionally high values of capacitance (more than double that of either component material) and rates of response illustrate the bulk property benefits to be gained from combining carbon nanotubes and conducting polymers on the nanoscale.

9:45 AM H5.4

ELECTRON AND LIGHT EMISSION FROM CARBON NANOTUBES AND CdS NANOWIRES. Jun Jiao, Lifeng Dong, David W. Tuggle, Jeremy Petty, Logan Love, Trenton J. McKinney, Portland State Univ., Dept of Physics, Portland, OR.

Due to quantum confinement effects, nanostructural semiconductors are expected to show distinctive optical and electronic properties from bulk materials. A number of nanocrystalline structures, such as carbon nanotubes and semiconductor nanowires, has been fabricated and studied. However, because of the difficulties of fabricating nanotubes and nanowires with controlled structural configurations, their electronic and optical properties are still debatable. Here we report the study of the electron field emission and light emission of carbon nanotubes and CdS nanowires. Carbon nanotubes used for this study were synthesized directly on the surface of tungsten or silicon substrates. The controlled growth of the nanotubes was achieved by using a focused ion beam (FIB) assisted localization of catalyst, with subsequent decomposition of hydrocarbon gas (C₂H₂) in a chemical vapor deposition reactor. The CdS nanowires were synthesized using the thermal evaporation of CdS powder with the presence of Au catalyst. This growth is controlled by the conventional vapor-liquid-solid (VLS) mechanism. The diameter, length, and growth directions of the nanotubes and nanowires were modified by varying different preparation parameters. The electron field emission of the nanotubes and nanowires was studied using a field emission microscope (with a base pressure $\sim 1 \times 10^{-8}$ Torr) equipped with a Faraday cup and a spectrum analyzer. The measurement suggests that at lower fields, the I-V (emission current vs. applied voltage) characteristic of the nanotube follows Fowler-Nordheim (F-N) emission behavior while at higher applied fields, current saturation appears. The spectrum analyzer was used to characterize the current fluctuations observed in the Faraday cup current. Power spectral densities with regions following various $(1/f)^n$ characteristics were

observed in the current fluctuations. During electron emission measurement, the field induced light emission of carbon nanotubes was observed as the applied voltages increased from 3100 V to 3700 V. The electron and light emission mechanisms of nanotubes and CdS nanowires will be discussed.

10:30 AM *H5.5

GRAPHITE-BASED ELECTRONICS. Claire Berger, Yan Yi, and Walt A. de Heer, School of Physics, Georgia Institute of Technology, Atlanta, GA.

Carbon nanotubes are currently actively investigated for their electronic applications potentials. We have recently found that carbon nanotubes are ballistic conductors at room temperature with mean free paths exceeding 50 μ m. Nanotubes found to be semiconductors or metals depending on their geometry and doping and innovative transistor prototypes have been demonstrated. These advances show that nanotubes may indeed have applications potential. On the other hand, it is not well known that the impressive electronic properties of nanotubes are common to other graphitic structures as well. We will present possible schemes to produce patterned graphite structures which function as active circuits. We also present recent attempts to lithographic pattern graphite in order to realize active nanographitic devices.

11:00 AM H5.6

GRAPHYNE NANOTUBES: NEW FAMILIES OF CARBON NANOTUBES. Vitor R. Coluci, Scheila F. Braga, Sergio B. Legoas, Douglas S. Galvao, Applied Physics Department, State University of Campinas, SP, BRAZIL; Ray H. Baughman, NanoTech Institute and Department of Chemistry, University of Texas at Dallas, Dallas, TX.

Carbon nanotubes have been object of great experimental and theoretical interest as evidenced by great amount of work carried out in the last years. Although nanotubes containing heteroatoms (N, B, etc.) have also been studied, new forms of carbon-based materials could represent a potential structural alternative for conventional carbon nanotubes (CNTs). One example of these forms is the graphyne, an allotropic form of carbon consisting of planar molecular sheets containing only sp and sp² carbons in the form of aromatic six-membered rings that are interconnected with acetylene groups. In this work we propose new families of carbon nanotubes based on graphyne motifs. In analogy with CNTs graphyne nanotubes would be formed rolling up graphyne sheets to form seamless cylinders. Electronic and structural properties were analyzed using tight-binding and ab initio density functional methods. Our results show that these graphyne tubes present richer structural and electronic properties than conventional nanotubes. The high porosity in the graphyne nanotubes shells would enable unprecedented shell doping, as well as rapid materials transport through the nanotubes sidewalls. Chemical stability and possible routes for synthesis are also addressed.

11:15 AM H5.7

FIELD EMISSION PROPERTIES OF BN/C AND BN@C NANOTUBES. Vincent Meunier, Thomas Zacharia, Oak Ridge National Laboratory, Oak Ridge, TN; Christopher Roland, J. Bernholc, North Carolina State University, Raleigh, NC; Marco Buongiorno Nardelli, North Carolina State University, Raleigh, NC and Oak Ridge National Laboratory, Oak Ridge, TN.

The discovery of carbon (C) nanotubes as a material with outstanding mechanical and electrical properties has led to a quest for other novel graphene-based structures with technologically desirable properties. The closely related boron (B) nitride (N) nanotubes and mixed BNC systems have electronic properties that are complementary to pure carbon nanotubes. The polarized B-N bond gives rise to important effects in the electronic properties of BN-doped carbon nanotubes. In particular, BN nanotubes possess a non-zero spontaneous polarization that makes them strong pyro- and piezoelectrics. BNC hybrids can exist in two distinct configurations: a quasi-1D BN/C heterostructure or a quasi-2D multi-walled tube with separate BN and C shells. In the former, the BN and C phases are covalently joined while they are segregated in the latter. In this talk, we show that the introduction of BN sections into carbon nanotubes leads to a large increase in the field emission properties at the carbon tip. This is due to the intrinsic electric field associated with the BN polar network, which induces a substantial reduction in the work function at the carbon tip. The change in the work function greatly improves the field emission properties, since the decrease in the work function exponentially increases the current density. Using state-of-the-art ab initio calculations, we show that this effect is present in both BN@C and BN/C systems. While the improvement is limited in the coaxial geometry, the current density is predicted to increase by up to two orders of magnitude in the BN/C systems.

11:30 AM *H5.8

METAL NANOWIRES ARRAYS FOR CHEMICAL SENSING.

Reg Penner, Department of Chemistry, University of California-Irvine, Irvine, CA.

A general method is described for the preparation of arrays of metal nanowires. Nanowires composed of noble or coinage metals including copper, nickel, gold, palladium and other metals with diameters in the range from 60 nm to 750 nm, were obtained by Electrochemical Step Edge Decoration (ESED); the selective electrodeposition of metal at step edges. Nanowire growth by ESED was accomplished on highly oriented pyrolytic graphite surfaces by applying three voltage pulses in succession: An oxidizing activation pulse, a large amplitude, reducing nucleation pulse, and a small amplitude reducing growth pulse. The activation pulse potential was optimized to oxidize step edges on the graphite surface just prior to deposition. The nucleation pulse had an overpotential for metal deposition of between -200 and -500 mV and a duration of 5-10 ms. The growth pulse had a small deposition overpotential of less than -100 mV. Nanowire growth was characterized by a time-independent deposition current and consequently, the nanowire radius was proportional to the square root of the deposition time in accordance with the expected growth law. The metal nanowire arrays prepared using this approach may be lifted off the graphite surface, and incorporated into chemical sensors. Examples of such sensors will be described in this presentation.

**SESSION H6: PHYSICS, CHEMISTRY AND
MODELING OF NANOSTRUCTURES**
Chairs: Lhadi Merhari and Thomas Orlando
Wednesday Afternoon, December 4, 2002
Room 309 (Hynes)

1:30 PM *H6.1

BIOLOGICALLY INSPIRED CONTROLS OVER ASSEMBLY OF CRYSTALLINE NANOSTRUCTURES. J.J. De Yoreo, C.A. Orme, S.R. Qiu, C.L. Cheung, Lawrence Livermore National Laboratory; P.M. Dove, K.J. Davis, Virginia Polytechnic Institute; M. Kurimoto, B. Kahr, University of Washington, Seattle, WA.

By utilizing small molecules, peptides, and proteins to modulate crystal nucleation and growth, living organisms produce topologically complex 3D single crystals and crystal composites. They exhibit control over the location, phase and crystallographic orientation of the nuclei, as well as the morphology and kinetics of the growing crystals. A common paradigm for interpreting this phenomenon asserts that the stereochemistry of the modifier is matched to that of a particular crystallographic plane that would not otherwise be expressed during nucleation or growth. Here we review the results of AFM-based investigations into the control of surface and solution chemistry on nucleation and growth in many crystal-impurity systems. We have utilized the AFM as a "dip-pen" to create chemical templates for nucleation and performed in situ imaging of growth during the introduction of both inorganic and organic impurities into the solution. The systems examined include carbonates, phosphates, oxalates, and phthalates nucleated on alkane thiol SAMs or grown in the presence of inorganic ions, amino acids, and organic dyes. In all cases, the growth kinetics and resulting crystal habit are defined by modifications to existing atomic steps and these modifications vary dramatically depending on the step direction, even on a single crystal face. While the exact mechanism of growth modification is different in each system, one common feature is that the important molecular-scale interaction that gives rise to growth modulation is between the impurity and a specific set of steps. These results show that, while control over nucleation may be understood within the paradigm of stereochemical recognition, to understand the controls on growth kinetics and morphology, a model that emphasizes the importance of step-specific impurity interactions on existing faces is more appropriate. This work was performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under contract No. W-7405-ENG-48.

2:00 PM H6.2

PHOTO-CONTROL OF NANO-INTERACTIONS IN MICROSYSTEMS. Nelson S. Bell, B.G. Potter, K. Simmons-Potter, Joe Thomes, John Lean, Chad Staiger, Doug Loy, and Greg Jamison, Sandia National Laboratories, Materials Chemistry, Albuquerque, NM.

The manipulation of physical interactions between structural moieties on the molecular scale is a fundamental hurdle in the realization and operation of nanostructured materials and high surface area microsystem architectures relying on phenomena such as self-assembly, fluid flow, and interfacial tribology. The introduction of reversible photo-tuned interactions by photosensitive molecular structures provides optical activation of nano-interactions impacting behavior on the nano- and microscales. We present observations on the surface characteristics of organic structures with known

photophysical effects and high probability for influencing target interaction processes. The properties of these photophysical groups are examined in the form of thin films, the rheology of photo-sensitive particles, and as colloidal crystal self-assembled photonic band gap structures. Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy under contract DE-AC04-94AL85000.

2:15 PM H6.3

ATTACHMENT OF GOLD NANOPARTICLES TO CARBON NANOTUBES BY CHEMICAL MANIPULATION. Kuiyang Jiang, Ami Eitan, Linda S. Schadler, Pulickel M. Ajayan, Mauricio Terrones*, Richard W. Siegel, Rensselaer Nanotechnology Center, Rensselaer Polytechnic Institute, Troy, NY; *Fullerence Science Center, CPES, University of Sussex, Brighton, UNITED KINGDOM.

Since their discovery in 1991, carbon nanotubes have been of great interest because of their unique structural, electrical and mechanical properties. Their potential applications include nanodevices, quantum wires, ultrahigh-strength engineering fibers, sensors, catalyst supports, etc. Moreover, carbon nanotubes have been used as a template to fabricate some intriguing nanostructures. In this study, we present the anchoring of gold nanoparticles to carbon nanotubes by chemical modification of the carbon nanotubes. IR and XPS studies confirmed the success of the chemical modification. TEM studies showed that well-dispersed gold nanoparticles decorate the walls and ends of the nanotubes. This also reveals that the functional groups on carbon nanotubes via chemical modification are present not only on the ends, but also along the length of the nanotubes. The approach used is simple and versatile, and can be used to attach many other nanoparticles (e.g., semiconductor nanocrystals, magnetic nanoparticles, etc.) to the carbon nanotubes.

2:30 PM H6.4

PHASE TRANSITIONS IN OCTANETHIOL-CAPPED NANOCUSTER ASSEMBLIES. A.V. Ellis, R. Goswami, K. Vijayamohan, Rensselaer Polytechnic Institute, Dept of Material Science and Engineering, Troy, NY; C. Ryu, Rensselaer Polytechnic Institute, Dept of Chemistry, Troy, NY; G. Ramanath, Rensselaer Polytechnic Institute, Dept of Material Science and Engineering, Troy, NY.

Monolayer-protected nanoclusters possess unique optoelectronic properties that can be tuned by adjusting the cluster composition, dimensions and capping layer chemistry. Interlinking these nanoclusters using molecular connectors to form 2D and 3D assemblies is of interest for harnessing these properties in creating larger length-scale devices. Here, we describe phase transitions in 3D assemblies of octanethiol (OT)-capped nanoclusters of Ag and Au and CdS of sizes ranging from 2 to 10 nm. We use a combination of differential scanning calorimetry (DSC), transmission electron microscopy (TEM), infrared spectroscopy (IR), thermogravimetric analysis (TGA) and in situ polarized microscopy (PLM) in our studies. DSC measurements reveal two melting-type reversible transitions at ~67 and 125°C in assemblies of OT-capped Ag nanoclusters, which are solids at room temperature. TEM of the assemblies show interlinked nanoclusters in a close-packed configuration, due to hydrophobic interactions between the OT caps. Neither the nanoclusters nor their assemblies show observable structural changes after thermal cycling, indicating that the phase transitions are due to OT. PLM and IR measurements show that the first transition corresponds to the melting of a phase comprised of excess OT i.e., those not attached to the nanoclusters. The second transition corresponds to the "melting" of the nanocluster assembly due to increased mobility of the OT molecules that cap and interact with alkyl chains attached to adjacent nanoclusters. Heating above 150°C leads to the disappearance of the phase transitions during subsequent cooling and heating, indicating desorption and breakage of OT caps. Unlike Ag-OT, Au-OT and CdS assemblies are liquids at room temperature. Au-OT shows only one reversible transition near 0°C, corresponding to the second transition described above, while CdS-OT shows no observable transitions between 20 and 250°C. We explain these results in terms of the strength of interactions between OT and the nanoclusters.

2:45 PM H6.5

CRITICAL UNIVERSALITY AND MAGNETIC PHASE TRANSITIONS OF A MODEL NANOCRYSTALLINE FERROMAGNET: A MONTE CARLO STUDY. Guang-Ping Zheng and Mo Li, School of Materials Science and Engineering, Georgia Institute of Technology, Atlanta, GA.

The critical scaling properties of a model Ising model is investigated using Monte Carlo simulations in the digital sample of an ensemble of nanocrystals. The effects of the microstructural properties (grain size, grain size distributions and grain boundaries are modeled using a new algorithm. Using the cluster algorithm, we calculated the

magnetization and magnetic properties of the model nanocrystalline sample. It is found that despite the shift of the critical temperature, all the critical exponents of Ising model remains the same as those in the pure system. The nanocrystalline Ising system, therefore, remains in the same universality class.

3:30 PM H6.6

SUPERCONFORMAL FILM GROWTH IN SUBMICRON FEATURES. T.P. Moffat, D. Wheeler, B. Baker and D. Josell, NIST, Gaithersburg, MD.

Electrodeposition of copper has been implemented in the fabrication of the latest generation of integrated circuits resulting in faster clock speeds, enhanced reliability and lower processing cost. Central to the success of the process is the ability to yield void and seam-free, bottom-up filling of high aspect ratio trenches and vias. Early models of "superfilling" assumed location-dependent growth rates derived from diffusion-limited accumulation of an inhibiting species. Such models were unable to predict several key experimental observations. Recently, a curvature enhanced accelerator coverage (CEAC) mechanism has been used to quantitatively predict superconformal electrodeposition of copper and silver in trenches and vias. The model provides a simple explanation for the long-standing observation of the smoothing action provided by certain electrolyte additives (traditionally referred to as "brighteners"). The construct has also been extended to quantitatively explain superconformal chemical vapor deposition (CVD).

3:45 PM H6.7

MODELING THE FLOW OF BINARY FLUIDS IN A PATTERNED MICROCHANNEL. Olga Kuksenok, Anna Balazs, Chemical Engineering Department, University of Pittsburgh, Pittsburgh, PA; David Jasnow, Physics Department, University of Pittsburgh, Pittsburgh, PA; Julia Yeomans, Theoretical Physics Department, Oxford University, Oxford, UNITED KINGDOM.

We develop a three-dimensional hydrodynamic model that reveals the thermodynamic behavior and flow patterns of a binary fluid moving over patterned substrates within a microchannel. The binary fluid consists of two immiscible components, A and B, that are subjected to a Poiseuille flow. We model patterned substrates by introducing domains with preferential wetting interactions for the A or B components. We investigate how the patterned substrate can be exploited to create additional interfaces between the A and B components and to yield relatively wide regions of mixed fluids inside the microchannel. We also isolate conditions that drive the periodic formation of a droplet on the neutral wall and the movement of the droplet along the channel. The droplet size and velocity strongly depends on the interfacial tension between the A and B fluids and the interaction with the patterned substrate. The results provide guidelines for controlling the fluid flow and for creating localized "mixing stations" within microfluidic devices.

4:00 PM H6.8

FINITE ELEMENT ANALYSIS OF NANOSCALE THERMAL MEASUREMENTS OF SUPERLATTICES. Jason R. Foley and C. Thomas Avedisian, Thermal Sciences Laboratory, Sibley School of Mechanical and Aerospace Engineering, Cornell University, Ithaca, NY.

Thermal wave techniques are widely used for characterizing the thermal properties of bulk materials and thin films. In the data analysis of these experiments, the samples are assumed to be effectively semi-infinite layered solids or infinite planar films, resulting in one- or two-dimensional heat flow. However, only certain sample geometries and experimental conditions satisfy these assumptions and, if violated, can lead to significant errors in the thermal property estimates, e.g., edge effects in micro- or nano-scale mesas or patterns. We present, for the first time, a finite element analysis for two- and three-dimensional heat flow in samples of arbitrary shape and composition. The finite element formulation is summarized and the governing differential equations for the heat transport are reviewed. Various boundary conditions are considered, including thermal boundary resistances at interfaces, applied heat fluxes, and insulated surfaces. Experimental data from bulk and nanofabricated material systems are presented and analyzed, with special attention to measurements of superlattices.

4:15 PM *H6.9

PROCESSING IN MATERIALS THAT MEDIATE THREE-DIMENSIONAL FABRICATION. H. Helvajian, Laboratory Operations, The Aerospace Corporation, Los Angeles, CA.

As feature size is reduced the material/compound that comprises the "building-block" unit must, with increasing relevance, participate in the assembly process. This is especially true in three-dimensional fabrication and for feature sizes accorded in nanofabrication.

Therefore, "reagent" materials or substrates that can be tailored to mediate in the material processing and fabrication will be more of a necessity. For fabricating features in the microns realm and for structures/devices that must be in glass or ceramic material, we have found a material that has this mediating effect. The material is a photostructurable glass ceramic, akin to ceramic kitchen flatware and processed much like that in photography. A laser with a wavelength that is tuned to material excitation is used to impregnate a 3D volume image in the glass substrate by a direct-write operation. The stored image can then be selectively etched in hydrofluoric acid. We have fabricated true 3D structures that have numerous applications in MEMS, microfluidics and mm-wave communications. These structures cannot easily be fabricated without resorting to countless masking steps. The current technique has size resolution down the micron level, but has the potential to go smaller. We will present the developed 3D material fabrication process, structures and devices fabricated in the microns feature size resolution realm and the approaches being taken to go lower.

4:45 PM H6.10

EVOLUTION OF CARBON SELF-ASSEMBLY IN COLLOIDAL PHASE DIAGRAM. Vaclav Bouda, Czech Tech Univ, Dept Mechanics and Materials Science, Prague, CZECH REP.

The growth of the self-assembled structure of carbon colloidal particles has been studied [1]. The system of carbon particles was processed in electrical field in polymer melt with controlled ionic concentration. Phase transitions of colloidal systems of carbon particles only have provided an effective interpretation of the complex evolution of the self-assembled structure of carbon particles. Interactions between doublets of CB colloidal particles are recently interpreted in terms of DLVO approximation of interaction energy of two blocks as multiples of average thermal fluctuation kT . Plots of the sum of energy of electrostatic repulsion and of energy of van der Waals attraction versus separation between the doublets show the energy barriers to coagulation of high B and the energy wells with the secondary minima of depth W. We suggest colloidal phase transitions at critical juncture of the concentration of ions and of the parameter of surface potential. Six transition lines enclose fifth phases of the assembly of carbon colloids: lateral vapor + axial vapor (VAPOR), lateral liquid + axial vapor (COLUMNAR LIQUID CRYSTAL), lateral liquid + axial liquid (SMECTIC LC), lateral liquid + axial solid (NEMATIC LC), and lateral solid + axial solid (SOLID). The model provides a tool to control the evolution of carbon self-assembly. For instance, the required carbon self-assembly with high specific surface area and high permittivity for super-capacitors can be induced in appropriate electrical field in a polymer melt with effective ionic concentration. References [1] Bouda, V., Chladek, J., Carbon Metamorphoses in a Medium with Varying Ionic Concentration. Mat. Res. Soc. Symp. Proc. Vol. 661, MRS 2001, p. KK5.17.1 - 6.

SESSION H7: POSTER SESSION
SYNTHESIS, PROPERTIES AND APPLICATIONS
OF 1D/2D/3D NANOSTRUCTURES
Chairs: Lhadi Merhari and David P. Taylor
Wednesday Evening, December 4, 2002
8:00 PM
Exhibition Hall D (Hynes)

H7.1

DIRECT NANOSCALE PATTERNING OF SOFT AND HARD MAGNETIC NANOSTRUCTURES VIA DIP-PEN NANOLITHOGRAPHY (DPN). Lei Fu, Vinayak P. Dravid, Dept. of Materials Science & Engineering; Xiaogang Liu, and Chad A. Mirkin, Dept. of Chemistry, Northwestern University, Evanston, IL.

Magnetic structures enjoy a wide variety of technological applications, and exhibit several basic and intriguing scientific phenomena. Other than the obvious applications of information storage, magnetic structures, especially at nanoscale, are becoming increasingly important in bio-detection, sensing and therapeutic fields. The advent of nanofabrication technology opens up new avenues to manipulate magnetic materials, and create novel architectures for engineering new materials, devices, and for obtaining better insight into micromagnetism. We have utilized the site- and shape-specific patterning capabilities of recently developed dip-pen nanolithography (DPN) approach to pattern soft and hard magnetic nanostructures. This is accomplished in two different but related ways. In first, DPN is used to pattern MHA templates that have affinity for oxide nanoparticles. Once these "sticky" patterns are created by DPN, the substrate is dipped in colloidal suspension of magnetic oxides (Fe_3O_4 , MnFe_2O_4) to allow colloidal nanoparticle binding to MHA-templates. In a second novel approach, sol-gel precursor for Barium ferrite ($\text{BaFe}_{12}\text{O}_{19}$) is used to directly pattern complex architecture on SiO_x substrate. The precursor pattern is then directly converted to hard

Ba-hexaferrite nanostructures under appropriate heat treatment. A variety of structural and magnetic measurements indicate the efficacy and efficiency of the approach. The presentation will cover the synthesis, patterning and characterization of magnetic nanostructures and argue that DPN-based approach present an alternate strategy for complex and hierarchical architecture for inorganic nanostructures.

H7.2
TEM ANALYSIS OF FIB PREPARED CROSS-SECTIONS OF THE ELASTOMER STAMPS AND IMPRINTED PATTERNS FOR NANO-LITHOGRAPHY. Richard Langford, Amanda Petford-Long, Oxford Univ, Dept. of Materials, Oxford, UNITED KINGDOM.

Current optical based lithography is now reaching its limits of resolution, while electron beam lithography is a serial process and so is inherently slow. Therefore, methods for nano-lithography, such as, micro-contact printing (MCP) and nano-imprint lithography (NIL), that offer low cost, high throughput processing are being developed. MCP involves curing an elastomer, normally polydimethylsiloxane (PDMS), onto a master and then using this as a stamp to transfer the "ink". NIL involves imprinting the master, usually into poly(methyl-methacrylate) (PMMA) and then using the patterned PMMA as a mask for subsequent processing. Here, we report on the use of a focused ion beam (FIB) system to prepare transmission electron microscopy (TEM) cross-sections of the masters, elastomer stamps and imprinted patterns. We show that the lift-out technique can be used to prepare cross-sections of both the elastomer stamps and the imprinted PMMA. As the FIB system can prepare the cross-sections to within 50 nm of a specific site this enables the same regions of the master, stamp and imprinted patterns to be cross-sectioned and therefore the pattern transfer and reproducibility to be assessed over the patterned area. The masters were prepared using a combination of e-beam lithography and conventional processing and focused ion beam milling. PDMS was used as the elastomer and PMMA for the nanoimprinting.

H7.3
FROM SELF-ORDERING TOWARDS IMPRINT LITHOGRAPHY: LARGE-SCALE SYNTHESIS OF MONODISPERSE NANORODS. Kornelius Nielsch, Jinsub Choi, Ralf B. Wehrspohn, Herbert Hofmeister, and Ulrich Gösele, Max-Planck-Institute of Microstructure Physics, Halle, GERMANY; Guido Sauer, Georg Brehm, and Siegfried Schneider, Institute of Physical Chemistry, University of Erlangen, GERMANY.

Monodisperse nanorods are highly desirable for many biomedical applications ranging from diagnostics of cancer cells to drug delivery. In the recent year, self-ordered alumina pore channel arrays, based on an approach of Masuda et al. [Science 1995, 268, 1466], have attracted a lot of interest as a template material for the synthesis of anisotropic nanoparticles with a defined diameter ($\pm 10\%$). In analogy to polycrystallites, the pore channels are hexagonally self-arranged in domains. In these pore arrays, numerous lattice defects and domain boundaries exist where large deviations of the average pore diameter occurs. When we introduce imprint lithography in the fabrication process of our templates, a monocrystalline arrangement of pore channels on a μm^2 -scale is obtained and the deviation of the pore diameter is reduced to less than 5%. We have developed a novel 4th imprint stamp consisting of hexagonal convex pyramid array based on modern VLSI processing using DUV-lithography, anisotropic etching, LPCVD Si₃N₄ deposition and wafer bonding. Using a commercial oil press the pattern of the imprint mold is directly transferred into polished aluminum substrates. Subsequently, the aluminum is anodized and a perfectly arranged array of highly monodisperse alumina pore channels is formed. The alumina templates are filled by electrodeposition or autocatalytic deposition with metals like Ag, Au, Co, Cu or Ni and - in contrast to most publications in this field - a degree of pore filling of almost 100% was achieved. The nanorod diameter (20...400 nm) and its length (0.2...50 μm) can be adjusted precisely over a large range. TEM characterisation shows that silver nanorods are single crystalline. The nanorods might be transferred into an aqueous solution by selectively dissolving the alumina matrix. The dissolved nanorods can be further functionalized or serve as templates for hollow polymer nanococoons.

H7.4
FORMATION OF CARBON NANOTUBES ON NICKEL FILMS/PARTICLES USING CVD. Stephanie Bazzana and Al Sacco Jr., Center for Advanced Microgravity Materials Processing, Department of Chemical Engineering, Northeastern University Boston, MA.

Carbon nanotubes (CNTs) are a possible material for field emission. One problem is that nanotubes are often produced from metal particles embedded in non-conducting surfaces (e.g., alumina/silica). This requires rearranging the nanotubes on a conducting surface for application. CNTs can be produced on a conducting media using

CVD and thin film nickel supports. CNTs were grown on thin nickel films of thicknesses below 5 nm. Thin nickel films were produced by evaporation at 9×10^{-7} Torr. These films were exposed to flowing hydrogen (20 mL/s, STP) at 1173 K. Their initial thickness controlled the height and diameter of the semi-hemispherical particles (sitting on a continuous nickel film) resulting from hydrogen exposure. As the thickness of the thin-film decreased from 5 nm to 1 nm, the height of the nickel particles decreased from 16 nm to 2 nm $\pm 10\%$, and the diameter decreased from 80 nm to 45 nm $\pm 10\%$. These nickel particles were exposed to a mixture of 5 gases including H₂, CO, CH₄, CO₂ and H₂O at 20 mL/s (STP) at 900 K and 1 atm. The gas phase carbon activity (\hat{a}_c) was controlled at 10, while the atomic ratio O/H in the gas phase was set at 0.1. SEM indicated that CNTs were observed on all samples. As the height and diameter of the particles became smaller, the diameter of the nanotubes decreased from 40 nm to a minimum value of approximately 20 nm $\pm 1.5\text{nm}$, at which point the density of nucleation diminished. Increasing (\hat{a}_c) to 20, while the other parameters remained constant, increased the nucleation and decreased the minimum diameter of the carbon nanotubes to 15 nm $\pm 1.5\text{nm}$. This suggests that control of the thermodynamic driving force for carbon deposition coupled with control of particle size can be used to generate uniform nanotubes for electron emitters.

H7.5
SYNTHESIS AND CHARACTERISATION OF CATALYST-FREE CARBON NANOTUBES FROM SILICON CARBIDE PRECURSORS. Elen S. Humphreys, Sung-Yoon Chung, John B. Vander Sande and Yet-Ming Chiang, Dept. of Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, MA.

Catalyst-free carbon nanotubes have been produced by the high temperature active oxidation of SiC. By selecting thermochemical conditions that promote the volatilization of SiO while maintaining local equilibrium in the graphite stability field, carbon nanotubes can be nucleated and grown from a variety of SiC precursors. In this study we used SiC powders of various particle sizes, and show that under suitable thermochemical conditions, particles of up to 10 micrometer diameter can be completely converted to densely-packed arrays of multiwall nanotubes. The resulting materials have been characterized using scanning electron microscopy (SEM), transmission electron microscopy (TEM) and Raman spectroscopy. These novel high-purity materials are found to contain a high proportion of aligned multi-walled carbon nanotubes with narrow diameters in the 2-10 nm range. Raman spectroscopic characterization of these high purity nanotubes, and their use in phage display experiments, are the topics of two other papers at this meeting. This research is supported by ONR Grant No. N00014-98-1-0354 and the DuPont-MIT Alliance.

H7.6
SIMPLE USE OF SiO₂ FILM THICKNESS FOR THE CONTROL OF CARBON NANO-TUBE DIAMETER DURING FERROCENE CATALYZED CVD GROWTH. Nitin Chopra, Bruce Hinds, Dept. of Chemical and Materials Eng., University of Kentucky, Lexington, KY; Padmakar Kichambare, Rodney Andrews, Center for Applied Energy Research, University of Kentucky, Lexington, KY.

Selective growth of carbon nano-tubes (CNT) on micron scale patterned substrates has been accomplished by taking advantage of the non-reactivity of ferrocene catalyst on alumina or H-terminated Si surfaces in a CVD process (Dali Qian Ph.D. dissertation 2001 University of Kentucky, Wei et al Nature 416, 495 2002). Demonstrated here is that this phenomenon can be used to control the diameter of CNTs when sufficiently narrow lines of SiO₂ surrounded by H-terminated Si are used. Narrow lines of SiO₂ (12-60nm) are formed at the cleaved or etched face of a Si/SiO₂/Si multilayer structure. This allows the precisely controllable thickness of a SiO₂ film to determine an exposed SiO₂ line width. There is no need for e-beam lithography since film thickness determines nm-scale line dimensions. CNTs are then formed by CVD with a ferrocene/H₂/Ar mixture at 700C. CNTs are observed to grow only on the exposed SiO₂ surface at the edge of the "mesa" structure. CNT diameters of 13.2, 20.5, 34.2, 64.3nm are observed for SiO₂ film thickness of 12, 19, 35, and 65 nm. Standard deviation are 1.1, 1.4, 3.8, 6.7 nm respectively. The larger distribution of CNT diameter with increased line width is consistent with wider SiO₂ linewidths not being able to affect smaller nucleation centers. Further investigations show improved control of diameter with etching technique as well as the successful use of self-assembly chemistry of iron catalyst for non-ferrocene catalyzed CNT growth by CVD. Resultant CNT diameter is directly related to catalyst support size. CNTs growing from this "mesa" edge process have applications for interconnections, NEMS or can be removed for later self-assembly into chemically defined structures.

H7.7
FIB-ASSISTED Pt DEPOSITION FOR CARBON NANOTUBE INTEGRATION AND 3-D NANOENGINEERING. K. Dovidenko, J. Rullan, K. Dunn, R. Moore, F. Heuchling. University at

Albany-SUNY, School of NanoSciences and NanoEngineering,
UAlbany Institute for Materials, Albany, NY.

Carbon nanotubes (CNTs) are potential candidates for a variety of new types of devices and some interconnect applications. High mechanical strength combined with good heat conductance and a range of attractive electrical properties make CNTs particularly interesting building blocks for rapidly emerging nanoelectronics and nanoengineering. For nanoscale devices based on carbon nanotubes, the performance will be crucially dependent upon the quality of the interfaces, since the entire device may now lie within nanometers of the interface. Successful integration of the nanotubes with metal aiming for application as an active part of a device or as a nano-wire, requires understanding of the effects of the metal fabrication process on the structure and chemistry of the nanotube, and on the stability of the CNT-metal interfaces. A Focused Ion Beam (FIB) instrument can be used to fabricate ultra-thin metal lines on carbon nanotubes to measure electrical properties or for integration and nanoengineering purposes. The quality of the interface between CNT and the metal contact line is of high interest, as the 30 kV focused Ga ion beam of the FIB can produce sufficient surface modification to affect the future device performance. We have used the FIB instrument to both fabricate the metal contacts and to make the electron-transparent samples across the Pt/CNT structure for further studies via transmission electron microscopy. Auger electron spectroscopy was used to characterize the composition of FIB-fabricated metal lines. The initial stages of FIB-assisted Pt deposition on multi-wall nanotubes are studied by transmission electron microscopy (TEM), electron energy loss spectroscopy, and energy filtered TEM. The effects of Pt deposition on the shape and composition of the top-most CNT layers as a function of FIB imaging and deposition parameters are presented. FIB parameters are optimized to provide the non-destructive imaging and controllable Pt deposition with minimal damage on the CNT.

H7.8
GROWTH OF WELL-DEFINED CARBON NANOTUBES ON ATOMIC FORCE MICROSCOPY PROBES SUITABLE FOR METROLOGY APPLICATIONS. Y.N. Emirov, J.D. Schumacher, M. Beerbom, University of South Florida; D.A. Walters, University of Central Florida; Z.F. Ren, Z.P. Huang, Boston College; B.B. Rossie, Agere Systems; and R. Schlaf, University of South Florida.

Well-defined carbon nanotubes (CNT) were grown on the apexes of standard Si atomic force microscopy cantilevers. CNT probes are thought to be ideal atomic force microscopy (AFM) probes for use in high aspect ratio critical dimension metrology (CDM). Their mechanical strength at small diameters makes them ideal probes for narrow and deep features. For these applications growth location, diameter, length and orientation of the CNT needs to be precisely defined. Already existing manually attached designs and CNT grown by standard chemical vapor deposition cannot satisfy these requirements. Our efforts demonstrate that the application of advanced focused ion beam (FIB) techniques in conjunction with plasma enhanced chemical vapor deposition (PECVD) offers a possible solution for achieving above design goals. Due to the interesting mechanical and electronic properties of CNT, this technology promises to have applications beyond AFM probes such as the development of CNT integrated electronic circuits or micro electromechanical devices (MEMS).

H7.9
BUILDING MACRO-SCALE NETWORKS AND BRIDGES OF ALIGNED CARBON NANOTUBES. Anyuan Cao, Bingqing Wei, P.M. Ajayan, G. Ramanath, Dept of Materials Science & Engineering, Rensselaer Polytechnic Institute, Troy, NY.

In order to harness the attractive properties of carbon nanotubes (CNTs) for future device applications, it is essential to create mesoscale architectures with CNT-metal contacts. Here, we demonstrate two bottom-up methods based on thermal chemical vapor deposition (CVD) to assemble cm-scale networks of mm-wide CNT stripes, and mm-scale bridges of aligned carbon nanotubes (CNTs) across metal contacts. Both methods are attractive for creating CNT-based multilayer and crossbar architectures, and are easily amenable to scaling to lower device dimensions as well as larger areas. In the first method, we use a two-step CVD process in which a patterned CNT film serves as a template for growing cm-long mm-wide CNT stripes. Track patterns of exposed silica are created in a blanket film with vertically aligned CNTs grown from a xylene/ferrocene mixture. In the second step, vertically oriented CNT stripes grow in these exposed regions and inherit the pattern configuration. The CNT templates can be selectively removed while retaining the crossbar-like networks of CNT stripes. In the second method, we assemble mm-scale bridges with cm-long multiwalled CNT bundles across metal contact structures. CNT bundles (average diameter < 50 nm) are synthesized by CVD from a

hexane-ferrocene-thiophene mixture. Each bundle consists of tens to hundreds of aligned CNTs. During the CVD process, the as-grown nanotube bundles are carried by gas stream to the end of the reaction quartz tube, where they deposit onto arrays of relief metal structures on silicon substrates and form macroscopic bridges. We show that the CNT bridges assemble across metals tips in soccer-goal-post and telephone-pole type configurations are aligned along the gas flow direction.

H7.10
VERTICAL ALIGNMENTS OF SINGLE-WALLED CARBON NANOTUBES ON CHEMICALLY FUNCTIONALIZED SILICON SUBSTRATES. Ha Jin Lee, Hyeyoung Park, Sunyoung Koo, Haiwon Lee, Hanyang University, Department of Chemistry, Seoul, KOREA.

A carbon nanotube has been widely investigated as an essential component for fabricating nanoelectronic devices and its numerous applications. We investigated the vertical alignments of single-walled carbon nanotubes (SWNTs) on chemically functionalized Si surfaces using chemical reactions between chemical groups in SWNTs and surfaces. For controlling the high selectivity of a specific chemical reaction, a pre-patterned 3-D nanostructure was used by using AFM anodization lithography for achieving the vertical alignment of SWNTs. To consider the further chemical reaction with chemically modified Si surface, the carboxylic acid groups were converted into acid chloride groups followed by the reaction with chemically functionalized surfaces. The protruded structures on pre-patterned areas strongly suggest the vertically oriented SWNTs, and the distribution of the vertically aligned SWNTs becomes denser and their heights are longer on the prolonged reaction time. The aspect ratio of SWNTs aligned on -OH functionalized surface is independent from the reaction time ($H/W = 0.2$). After random alignment of relatively shorter nanotubes on the substrate, their bundle size increases with increasing the reaction time due to strong van der Waals interaction between the lateral sides of nanotubes described as "nucleation growth". Longer tubes get also adsorbed on the surface by increase in the bundle size and nanotube length, simultaneously. Based on the chemical reactions of the modified SWNTs with functionalized surfaces, selective attachments of SWNTs were carried out onto pre-patterned surfaces. Detailed characterization of aligned SWNTs will be discussed.

H7.11
CONTROLLED DEPOSITION AND APPLIED FIELD ALIGNMENT OF SINGLE WALLED CARBON NANOTUBES FOR CNT DEVICE FABRICATION. Jan Smits, Lockheed Martin Space Operations, Hampton, VA; Buzz Wincheski, NASA Langley Research Center, Hampton, VA; JoAnne Ingram, Swales Aerospace, Hampton, VA; Neal Watkins, Swales Aerospace, Hampton, VA; Jeffrey Jordan, NASA Langley Research Center, Hampton, VA.

Carbon nanotubes (CNTs) offer great potential for advanced sensing devices due to their unique electronic transport properties. However, a significant obstacle to the realization of practical CNT devices is the formation of controlled, reliable and reproducible CNT to metallic contacts. In this work, a procedure for the deposition and alignment of CNTs onto metallic electrodes using chemically functionalized lithographic patterns is reported. This method uses photo and electron beam lithography to pattern simple Cr/Au thin film circuits on oxidized Si substrates. The circuits are then re-patterned with a self-assembled monolayer (SAM) of 3-aminopropyltriethoxysilane (APTES) to specify desired CNT locations between electrodes. The application of an applied electric field to the metallic contacts during the deposition of solution suspended single walled CNTs causes alignment of the CNTs in the field direction. This method consistently produces aligned CNTs in the defined locations. Application of this deposition method to the fabrication of CNT based sensor material is also presented.

H7.12
Abstract Withdrawn.

H7.13
Transferred to H5.3

H7.14
HYDROPHOBIC ATTACHMENT OF GOLD NANOCCLUSERS TO CARBON NANOTUBES. K. Vijayamohan, Materials Science and Engineering Dept, Rensselaer Polytechnic Institute, Troy, NY; A.V. Ellis, Materials Science and Engineering Dept, Rensselaer Polytechnic Institute, Troy, NY; R. Goswami, Rensselaer Polytechnic Institute, Troy, NY; N. Chakrapani, Materials Science and Engineering Dept, Rensselaer Polytechnic Institute, Troy; L.S. Ramanathan, Chemistry Dept, Rensselaer Polytechnic Institute, Troy, NY; P.M. Ajayan, G. Ramanath, Rensselaer Polytechnic Institute, Troy, NY.

Creating hybrid molecular units consisting of different kinds of nanoscale blocks is of interest for building new quantum-electronic devices and networks. Carbon nanotubes (CNTs) linked with nanoclusters is a striking example of such a unit that will allow the exploration and tuning of unique electrical and/or optical properties of nanotubes and 3D quantum dots. Here we demonstrate for the first time using high resolution transmission electron microscopy (HTREM), optical absorption spectroscopy (OS) and Fourier transform infrared transmission spectroscopy (FTIRTS) the attachment of Au nanoclusters to CNTs via hydrophobic interactions between self-assembled molecular monolayers of octanethiol molecules capping the nanoclusters, and acetone molecules activating nanotubes surfaces. HRTEM and OS measurements show that interlinked assemblies of Au nanoclusters with average size of ~ 3 nm are attached to the multiwalled CNTs treated with acetone. The Au nanoclusters retain a strong surface-plasmon peak after attachment and repeated washing, indicating robust interlinking and the preservation of the optical and electronic properties of the nanoclusters. These assemblies have discrete intercluster spacings with a preferred length corresponding to about one to two times the length of the octanethiol molecule, suggesting molecular interdigitation. This and the decreased flexibility of the octanethiol, indicated by FTIRTS, indicate strong hydrophobic interactions with the surrounding octanethiol molecules and acetone adsorbed on the surface. Results of our experiments with CNTs that were not treated with acetone showed no observable cluster attachment, emphasizing the importance of surface chemistry of the CNTs to create hybrid structures using molecular connectors. Based upon these results, we present a phenomenological model to explain the salient features of hydrophobically linked nanocluster-nanotube hybrid molecular units and assemblies.

H7.15

NANOSTRUCTURED MATERIALS ON CARBON NANOWALL TEMPLATES. Yihong Wu, National University of Singapore, Dept of Electrical and Computer Engineering, Singapore and Data Storage Institute, SINGAPORE; Bingjun Yang, National University of Singapore, Dept of Physics, Singapore and Data Storage Institute, SINGAPORE.

Recently we have succeeded in growing well-aligned two-dimensional carbon nanostructures dubbed carbon nanowalls.^{1,2} The nanowalls exhibit a remarkably different surface morphology as compared to fullerenes and carbon nanotubes, in particular their two-dimensionality and high surface area. Under typical growth conditions, the as-grown nanowalls have a thickness of several nanometers, a width of sub-micron, and a height of several microns. In-between the nanowalls there exist empty spaces of sub-micron dimensions. The unique surface morphology of carbon nanowalls makes them an ideal template for fabricating a class of mesoporous materials which may have applications in batteries, gas sensors, catalysts, and light emission / detection, field emission and biomedical devices. The results on the growth of Ni, NiCoFe, Fe, ZnO, TiO₂, InO₂, Au, Cu, and other materials will be reported in the meeting. All these materials form conformally on the nanowalls, resulting in pseudo-3D nanostructures. The application of some of these materials as gas sensors and electrodes for supercapacitors is also being explored. 1. Wu YH, Qiao PW, Chong TC, and Shen ZX, *Adv. Mater.* 14 (1): 64-67 JAN 4 2002. 2. Wu YH and Yang BJ, *Nano Letters* 2 (4): 355-359 APR 2002.

H7.16

EFFECT OF SITE DENSITY OF ALIGNED CARBON NANOTUBES ARRAY ON ELECTRIC FIELD SCREENING. Yi Tu, Zhongping Huang, Dezhi Wang, Zhifeng Ren, Dept of Physics, Chestnut Hill, MA.

Electric field screening has been observed in the densely packed carbon nanotube arrays. In this report, we show that CNTs arrays with different site density have been grown from Ni dots made by electrochemical deposition by plasma enhanced chemical vapor deposition. Field emission properties of CNTs arrays with site density from 10^6 to $10^9/\text{cm}^2$ and length of 1, 5, 10 μm have been studied.

H7.17

Abstract Withdrawn.

H7.18

FABRICATION OF CARBON NANOTUBE LATERAL FIELD EMITTERS. A.S. Teh, K.B.K. Teo, Manish Chhowalla, W.I. Milne, G.A.J. Amaratunga, Cambridge University, Engineering Dept., Cambridge, UNITED KINGDOM; S.-B. Lee, H. Ahmed, Cambridge University, Cavendish Laboratory, Cambridge, UNITED KINGDOM.

Recent progress in carbon nanotube synthesis has made it possible for a carbon nanotube to be grown vertically, as well as laterally, on a substrate at designated sites, making possible application of carbon

nanotubes as nanoelectronic components. However, there is a drawback in carbon nanotubes, which limits application to large-scale integrated devices. Although a method has been developed to selectively destroy metallic nanotubes, leaving only semiconducting ones, there is no known method of controlling the chirality of carbon nanotubes during synthesis, making it difficult to select semiconducting carbon nanotubes with a fixed energy gap for high-density integrated circuit application. Therefore it may be useful to have a device that does not rely on the transport properties of the carbon nanotubes but still delivers switching capability with gain. One such device is the carbon nanotube gated field emitter. It utilizes the geometric enhancement of the nanotube tip structure and the high current density transport capabilities of the carbon nanotubes. Here we report on the fabrication and operation of a lateral carbon nanotube field emitter. Compared to vertical field emitters using carbon nanotube cathodes, it has less alignment problems since the anode is fabricated at the same time as the cathode and the gates, and also may have reduced leakage since the electrodes are well separated. We use thermally oxidised Si as the substrate. Initially, Cr/Au alignment marks are deposited to use as reference markers. Then a thin layer (50-100 nm) of Al is evaporated, which will act as the sacrificial layer. Multi-wall carbon nanotubes (MWCNTs) were synthesised by plasma-enhanced chemical vapour deposition and dispersed on the surface. Electron beam lithography is used to define the anode, gates and the cathode contacts of the device. After Cr/Au metal deposition and lift-off the sacrificial Al is etched away leaving the nanotube suspended. The device turn-on voltage was ~ 11 V. The emission characteristics exhibit Fowler-Nordheim behaviour, which is a strong evidence of field emission. We will further investigate the characteristics of gate dependent operation of the device and also look at the performance of the devices with differing dimensions and carbon nanotube diameters.

H7.19

FIELD EMISSION FROM RUTHENIUM CONTAINING MULTIWALLED CARBON NANOTUBES. Padmakar Kichambare, Dali Qian, David Jacques, Rodney Andrews, University of Kentucky, Center for Applied Energy Research, Lexington, KY.

Among the types of materials investigated for field emitters, multiwalled carbon nanotubes (MWNTs) are well suited for display applications as their structure lends itself to easy fabrication on nanometer scale. Hence, tremendous efforts are being directed to achieve high electron emission current density at low applied voltage from the MWNTs. However, the poor emission current stability of MWNTs has hampered their prospect in field emission display devices. One of the easiest way of improving emission current stability would be the doping of the MWNTs. We report on the growth and field emission properties of Ru containing MWNTs, prepared by chemical vapor deposition (CVD) on Si(100) substrates. A mixture of ferrocene and ruthenocene (6:1) in xylene was used for the growth of Ru containing MWNTs. Scanning electron microscopy (SEM) reveals that Ru containing MWNTs are quasi-aligned with thicker root ends (outer diameter ~ 40 nm) and thinner tip ends (outer diameter ~ 15 nm). Some of these nanotubes form the nanotube chain structures in which the second segment grows from the tip of previous segment. The characteristic current-voltage measurements of Ru containing MWNTs demonstrate a low turn-on field of 11 V/ μm . The field emission current density in excess of about 14 mA/cm² at an applied field of 20 V/ μm has been achieved. A stable emission current density under a constant applied voltage has been observed. These investigation indicate that Ru containing MWNTs film could be a very promising for field emission devices.

H7.20

Zn_{1-x}Mg_xO NANORODS VIA MOLECULAR BEAM EPITAXY. Young Woo Heo, V. Varadarajan, K. Kim, Michael Kaufman, David Norton, University of Florida, Dept. of Materials Science and Engr, Gainesville, FL; Matthew Chisholm, Solid State Div., Oak Ridge National Laboratory, Oak Ridge, TN.

We recently reported on the growth of single crystal ZnO nanorods using catalysis-driven molecular beam epitaxy. ZnO nanorod nucleation was achieved via nucleation on Ag nanoparticles that are distributed on a SiO₂-terminated Si substrate surface. In this talk, we will describe recent results for the growth of the Zn_{1-x}Mg_xO nanorods. The modulation of the bandgap in compound semiconductors is a key issue in heterojunction formation for electronic and optical devices. In epitaxial thin films, the bandgap of ZnO ($E_g=3.37\text{eV}$) can be modified via alloying with MgO. Photoluminescence of Zn_{1-x}Mg_xO nanorods shows a peak shift to higher energy with increasing Mg, indicative to an increasing bandgap. The synthesis and properties of these structures will be reported, including photoluminescence, microstructure, and TEM data. The site-selective, in situ formation of ZnO-related nanorods and nanowires may prove attractive for nanodevice concepts.

H7.21

ZnO NANOWIRE GROWTH ON VARIOUS SUBSTRATES BY CVD THROUGH VAPOR-LIQUID-SOLID CRYSTAL GROWTH MECHANISM. Hyun-Gi Hong, Jung Inn Sohn, Youn-Su Kim, Seonghoon Lee, Department of Materials Science and Engineering, Kwangju Institute of Science and Technology (K-JIST), Kwangju, KOREA.

We have grown zinc oxide nanowires on silicon, sapphire, and gallium nitride substrates by thermal chemical vapor deposition (CVD) and investigated their structural and optical properties, using scanning electron microscopy, transmission electron microscopy, X-ray diffraction, and photoluminescence (PL) spectroscopy. The Au catalyst metal films are deposited on various substrates by a pulsed laser deposition technique under a pressure of 10^{-6} Torr. We found that the metal thin film was broken to nanoparticles during the CVD growth. Controlling the size of nanoparticles, we adjusted the diameter of nanowires. We generated zinc and oxygen vapor through carbothermal reduction reaction, and ZnO nanowire were synthesized on a substrate with a vapor transport process via catalyzed crystal growth at a temperature of 900°C or 950°C through vapor-liquid-solid crystal growth mechanism. The orientation of ZnO nanowires showed strong dependence on substrates. We investigated the dependence of the orientation and alignment of ZnO nanowires on a substrate, using SEM and TEM. Especially, gallium nitride substrate among substrates we used, is good for aligning zinc oxide nanowires. The size of ZnO nanowires is 20 to 100 nm in diameter and a few micrometers in length. From the analysis of XRD pattern, we found that ZnO nanowire is a wurtzite structure. PL spectra of ZnO nanowire were measured with a He-Cd laser (325 nm) of excitation power of 20 mW. Strong band-gap edge emission at 379 nm with a full width at half maximum (FWHM) of 52.09 meV was observed.

H7.22

CONDUCTING NANOWIRES AND NANOTUBE MATERIALS PREPARED FROM POLYMER FIBER TEMPLATES. Hong Dong, Verrad Nyame, Frederick Ochanda, and Wayne E. Jones Jr., Chemistry Department and Institute for Materials Research, State University of New York at Binghamton, NY.

The preparation of well-defined nanomaterials using template methods is well established in the materials literature including porous ceramics, open-framed layered structures, and thin films. In an effort to prepare novel thermally and electrically conducting materials, we have recently prepared extremely low dimensional conducting nanowires and fibers from conducting polymers (e.g. polyaniline, polypyrrole) using an electrostatic, non-mechanical "electrospinning" method. Insulating Poly(L-lactide) (PLA) fibers with average diameter of 200-700 nm were initially fabricated as core materials. The fibers were subsequently coated with thin 50-100 nm films of polyaniline or polypyrrole by in-situ polymer deposition methods. Upon relatively mild thermal treatment under inert atmosphere the PLA core fibers decompose leaving conducting tubes as demonstrated by SEM. The greatly enhanced surface to volume ratio of these materials is predicted to yield enhanced sensitivity compared with thin films prepared on substrates. Further, using more aggressive thermal treatments or the application of electroless plating stable conducting nanotubes of metals (e.g. Au, Cu) or graphite can be prepared suitable for use as thermal or electrical conductors in nanodevice applications.

H7.23

UNIDIRECTIONALLY ORIENTED NANORIBBON-DYE HYBRID MATERIALS CREATED BY SELF-ASSEMBLY AND ELECTROPHORESIS. Leiming Li, Guizhong Zhang, John C. Stendahl, Eugene R. Zubarev, and Samuel I. Stupp, Department of Materials Science and Engineering, Department of Chemistry, Medical School, Northwestern University, Evanston, IL.

Dendron rodcoil (DRC) molecules contain covalently connected dendritic, rod-like, and coil-like segments, and form gels with certain solvents like styrene or 2-ethylhexyl methacrylate (EHMA). Gelation is triggered by the self-assembly of DRC molecules into a network of ribbon-like nanostructures that are 10 nm wide, 2 nm thick, and up to 10 microns long. When subject to a DC electric field, electrophoresis occurs in the DRC-EHMA gel, creating thin solid films consisting mostly of DRC nanoribbons oriented preferentially along the poling direction. Small weight percentage of certain dye molecules, such as disperse red 1 (DR1), was dissolved in the gel. Similar electrophoresis creates hybrid films of unidirectionally oriented DRC nanoribbons and DR1 molecules. Strong emission polarization was obtained from the embedded DR1 dyes, significantly larger than that obtained from DR1-polystyrene control samples stretched up to 22 times their original length. Interestingly, no obvious decrease in emission polarization was observed after the oriented nanoribbon-DR1 films were annealed at 100°C.

H7.24

THERMOELECTRIC NANOWIRES BY TEMPLATE SYNTHESIS: FABRICATION, CONTACTS AND PROPERTIES. Oded Rabin^a, Yu-Ming Lin^b, Stephen B. Cronin^c, Gang Chen^d, Mildred S. Dresselhaus^{b,c}, Massachusetts Institute of Technology, ^aDept. of Chemistry, ^bDept. of Electrical Engineering and Computer Science, ^cDepartment of Physics, and ^dDept. of Mechanical Engineering, Cambridge, MA.

Using the technique we have developed to grow porous alumina templates on the surface of silicon wafers, we have fabricated arrays of nanowires of thermoelectric materials. By this method we can control the in-plane geometry by the design of the template and the substrate, and the out-of-plane dimension by control over the electrochemical nanowire growth process. We use several straight forward methods to make electrical contacts to the nanowires. Our transport studies show that both the structure of the nanowire and the contact region have a strong influence on the observed properties of the arrays.

H7.25

Abstract Withdrawn.

H7.26

RATIONAL CONTROL OF NANOSCALE HELICAL MORPHOLOGIES THROUGH BINARY SELF-ASSEMBLY. George John, Jong Hwa Jung, Kaname Yoshida, Hiroyuki Minamikawa, Toshimi Shimizu, CREST, Japan Science and Technology Corporation, Nanoarchitectonics Research Center, National Institute of Advanced Industrial Science and Technology, Tsukuba, JAPAN.

Mixed components of cardanyl glucoside derived from renewable resources provided nanotubes on self-assembly in water while the saturated homologue generated twisted fibrous morphology. The cardanyl glucoside mixture was fractionated into individual four components to study their contribution to the nanotube formation. The rational control of self-assembled helical morphologies has been achieved by binary self-assembly of the saturated and monoene derivatives. This method can provide the generation of a diversity of self-assembled high-axial-ratio nanostructures (HARNs), ranging from, twisted ribbons, helical ribbons and nanotubes.

H7.27

SYNTHESIS BY SELF-ASSEMBLY OF IRON-COBALT NANO-ALLOYS. Melissa Zubris, Rina Tannenbaum, Georgia Institute of Technology, School of Materials Science and Engineering, Atlanta, GA.

Nanoalloys, i.e. alloys formed via the co-aggregation of different metals at the nanoscale, represent an exciting new area in nanotechnology. These nanoalloys have unique properties that neither the bulk alloys, nor the discrete atoms possess. Gold and silver nanoclusters have been used to produce nanoalloys, but no such systems have yet been reported with transition metals. In this paper we are proposing the synthesis of iron and cobalt nanoalloys via the co-decomposition of iron and cobalt carbonyls. Zero-valent iron and iron oxide clusters that are produced via this decomposition exhibit excellent magnetic properties. Combining these iron nanoclusters with cobalt nanoclusters will form new nanoalloy compositions with good magnetic properties and interesting potential applications. In order to form iron-cobalt nanoalloys with no preferential aggregation of metal atoms resulting in phase segregation, the decomposition kinetics of the iron pentacarbonyl and dicobalt octacarbonyl precursors had to be firmly established. The kinetics of cobalt cluster formation via dicobalt octacarbonyl decomposition have been thoroughly investigated, but data for iron pentacarbonyl decomposition is relatively scarce. To fully understand the formation of the iron nanoclusters, a kinetic study was performed varying carbonyl concentrations and reaction solvents in order to establish reaction order and rate constants. This decomposition was performed in the presence of a polystyrene matrix, since the polymer attaches to the surface of the cluster, restricting the amount of metal-metal interactions that may occur, thus limiting cluster size. The studies presented in this work have established this decomposition to be a higher order process (not first order as previously assumed), with a complicated intermediate mechanism, which has been experimentally verified. By using this kinetic data, we will be able to predict the necessary conditions for the creation of new in-situ iron-cobalt nanoalloys using carbonyl precursors.

H7.28

ORGANIC MOLECULES ACTING AS TEMPLATES ON Cu(110). Federico Rosei, Y. Naitoh, M. Schunack, E. Legsgaard, I. Stensgaard, and F. Besenbacher, Physics Department and I-NANO, University of Aarhus, DENMARK; P. Jiang, A. Gourdon, and C. Joachim CEMES - CNRS Toulouse, FRANCE.

Large organic molecules have recently attracted interest from a fundamental point of view and for prospective applications in nanoelectronics, since they are the basic building blocks for molecular electronics devices [1]. We investigated the adsorption of Lander molecule [2] (C90H98) on Cu(110) by Scanning Tunneling Microscopy (STM) in the temperature range 100 - 300 K. The Lander has a central polyaromatic molecular wire (conducting backbone), and four "spacer legs" (3,5-di-tert-butylphenyl) for isolation from the substrate. The four legs are imaged with 3 different conformations by STM. Manipulation experiments with the STM at low temperatures on isolated Lander molecules adsorbed on step edges reveal a restructuring of Cu steps [2]: when removed from a step, a tooth-like nanostructure appears. The structure's width is two atomic rows, corresponding to the distance between the spacer legs within the molecule. This process is thermally activated: repeating the same manipulation experiments on molecules adsorbed at low temperatures (150 K), no restructuring of the Cu step edges is found. In a second set of experiments, the clean Cu(110) surface was exposed to oxygen to form oxygen induced (2x1) reconstruction surface. By dosing a proper amount of O₂ at 350 K we nanopatterned the substrate into Cu troughs along the [001] direction with 2 nm width, with a periodicity of about 5 nm. When Lander molecules are deposited on this template, they preferentially adsorb on bare Cu regions. By tuning molecular coverage in a controlled manner we obtained long rows of 1 D molecular nanostructures. This type of forced self-assembly opens new possibilities for ordering organic molecules on surfaces. References. [1] C. Joachim, J.K. Gimzewski and A. Aviram, Nature 408, 541 (2000). [2] F. Rosel et al., Organic molecules acting as templates on Metal Surfaces, Science 296, 328 (2002).

H7.29

SELF-ASSEMBLY OF METAL-OXIDE NANOSTRUCTURES: OXIDATION OF Cu FILMS BY IN-SITU UHV-TEM.

Guangwen Zhou, Judith C. Yang, Materials Science and Engineering Dept, University of Pittsburgh, Pittsburgh, PA.

The universal response of metal surfaces exposed to oxygen-bearing atmospheres is to oxidize. The oxidation product may be a thin protective adherent film or oxide islands depending on the oxidation conditions. The structural changes of the oxides are dependent on the complex kinetics and energetics of the particular materials system and the oxide morphology is controlled by kinetic and thermodynamic factors during the oxidation process. In-situ observations can provide insights into distinguishing between morphologies due to kinetic or thermodynamic considerations. It is reasonable to expect that temperature would affect the kinetics and/or energetics of the oxide formation. We have systematically investigated the dramatic effect of temperature on the oxide formation due to in situ oxidation of Cu(001) and modeled some of the morphology changes. We demonstrated that dramatically different morphologies of oxide nanostructures can be achieved by modifying the oxidation temperature. Quasi-one-dimensional Cu₂O structures with aspect ratios as large as 40:1 were formed at the oxidation temperature of 600°C. The in-situ observation data on the elongation of Cu₂O islands agree with the energetic calculations based on the balance between surface and interface energies and the elastic stress relaxation in the three dimensional islands. We developed a kinetic model based on oxygen surface diffusion that fits well with the observed volume evolution of the Cu₂O islands. The oxide volume increases parabolically before the shape transition, and exponentially afterwards, with respect to oxidation time. A peculiar pyramid structure, hollow Cu₂O terraced-pyramids, was formed when we oxidized Cu(100) films with thickness of 700 Å at temperature of 1000°C. The formation of terraces and empty space within the pyramid results from the sliding of the blocks of the island over one another on the slip system of {111}[110] to release the compressive strain exerted on the island due to the large volume change accompanied with oxidation of Cu to Cu₂O.

H7.30

A GENERALIZED FLUID-FORMING METHOD FOR SELF-ASSEMBLY OF PARTICLES INTO PLANAR ARRAYS.

X. Liu, Dept of Ceramic and Materials Engineering, Rutgers, the State University of New Jersey, Piscataway, NJ; E.F. McCandlish, Ceramar Corporation, New Brunswick, NJ; F. Cosandey, K. Mikulka-Bolen, Dept of Ceramic and Materials Engineering, Rutgers, the State University of New Jersey, Piscataway, NJ; L.E. McCandlish, Ceramar Corporation, New Brunswick, NJ; R.E. Riman, Dept of Ceramic and Materials Engineering, Rutgers, the State University of New Jersey, Piscataway, NJ.

Self-assembly of objects with different sizes and shapes into complex systems has excellent potential for application in microelectronics, optics, magnetics and microelectromechanical systems. We have developed a fluid-forming process for self-assembly of particles into planar arrays. The process operates on particles whose sizes range from nanometers to millimeters. Particle morphology can be used to

control the orientation of the particles within the arrays. For oriented-particle arrays, we have explored the use of cube-shaped particles. Randomly-oriented particle arrays can be processed using spherical particles. All of these fluid-formed arrays can be transferred onto a wide range of substrates to make monolayer or multi-layer structures. This presentation will focus on the preparation of < 001 >-orientated Pb(Zr,Ti)O₃ arrays using cube-shaped particles. Field emission scanning electron microscope (FESEM) and imaging analysis results showed that the cube arrays contained dense-packed (~80-90%) particles in the x-y plane. High-resolution X-ray diffraction (HRXRD) analysis and electron backscatter diffraction (EBSD) analysis revealed the crystallographic orientation of the cube particles, which were found to be randomly oriented in the x-y plane with their < 001 > directions oriented along the plane normal. These dense-packed < 001 >-oriented PZT planar arrays can be further processed as textured composites or textured single-phase materials.

H7.31

THE DEVELOPMENT OF THE CONTROL OF MORPHOLOGY TITANIA BASED PHOTONIC BANDGAP STRUCTURES.

Bonnie Gersten, Samuel Hirsch and Jennifer Synowczynski, Processing and Properties Branch, WMRD, US Army Research Laboratory, Aberdeen Proving Grounds, MD.

Recently, mono-sized spherical titania has been of interest as colloidal crystals for photonic band gaps due to their large refractive index in the optical regime ($n \sim 2.5$). In order to obtain the photonic crystal the particles need to be grown with as little as 5% error. They are typically assembled into photonic band gap structures (e.g., FCC) by self-assembly processes by one of the following methods: confined assembly, sedimentation growth or electrostatic interactions. Therefore, there is a need of controlling the size and shape of these oxide materials. In this paper we report the development of morphology control of titania by wet chemical methods so as to produce spherical sub-micron and micron size titania. The method of preparing these materials and characterizing by SEM and light scattering methods will be discussed.

H7.32

THE IMPORTANCE OF NOTHING IN NANOARCHITECTURES.

Debra R. Rolison, Jeffrey W. Long, Erik M. Lucas, Christopher P. Rhodes, Jeremy J. Pietron, Jean Marie Wallace, Wendy S. Baker, Rhonda M. Stroud, Naval Research Laboratory, Washington, DC.

The innate pore-solid architecture of aerogels, which are low density, innately nanoscale, highly porous materials, melds high surface area for heterogeneous reactions with a continuous, porous network for rapid diffusional flux of reactants and products. These advantages have previously been explored with aerogel-derived heterogeneous catalysts, but they are also relevant for sensors and for electrocatalysts when the aerogel can be made electrically conductive. Conductivity can be achieved by synthesizing conductive oxides, such as manganese oxide or by conformal deposition of nanowires atop the non-conductive network of a silica aerogel. We have also developed a flexible and general synthetic route in which silica (or in some instances, titania) sol serves as a nanogel to produce a diverse range of composite aerogels incorporating particulate guests. Particles ranging in size over six orders of magnitude (from a nanometer, which is smaller than the domain size of the silica, to a millimeter) can be accommodated in the aerogel host. The chemical nature of viable guests ranges from metal to metal oxide, carbon, ceramic and semiconductor to polymeric and biomolecular. The resulting composite is a material in which each phase can be independently tailored as needed. A hierarchical architecture with all the appropriate reaction, electrical, electrochemical, bioactivity, or catalytic requirements, including high surface areas readily accessed by molecular reactants, may now be assembled on the benchtop.

H7.33

SYNTHESIS AND PROPERTIES OF HYDROGEL CRYSTALS.

Xihua Lu, Zhibing Hu, University of North Texas, Dept of Materials Science and Physics, Denton, TX.

Novel hydrogels with mesoscopic crystal structures have been synthesized and characterized. First, monodisperse N-isopropylacrylamide (NIPA) co- 2-hydroxyethyl acrylate (HEAc) hydrogel nanoparticles were made using emulsion polymerization. And then hydrogel crystals were created by covalently bonding the self-assembled nanoparticles using crosslinker divinylsulfone (DVS). The inter-nanoparticle covalent bondings contribute to the stability of crystal structure, while self-assembly provides crystal structures that diffract light, resulting different colors. As a result, the novel hydrogel crystals, which contain up to 98 wt % water, display a striking iridescence like precious opal but soft and flexible like gelatin. The novel nanostructured hydrogels demonstrated the good mechanical

strength and thermal stability of crystal structures. The hydrogel crystals may find applications in many areas such as sensor, display, and biotechnology.

H7.34

DEVELOPMENT OF METAL-SILICA NANOCOMPOSITES IN A SINGLE STEP PROCESS BY THE POLYMERIZABLE COMPLEX METHOD. E.R. Leite, N.L.V. Carreo, E. Longo, J.F.R. Bachega and F.M. Pontes, CMDMC-LIEC, Departamento de Química, UFSCar, São Carlos, SP, BRAZIL; A. Barison, A.G. Ferreira, Departamento de Química, UFSCar, São Carlos, SP, BRAZIL; J.A. Varela, Instituto de Química, UNESP, Araraquara, SP, BRAZIL.

This work presents the synthesis and characterization of SiO_2 :metal (Ni, Co, Ag and Fe) nanocomposites processed by the Polymerizable Complex Method. The polymeric precursor solutions obtained were characterized by means of FT-Raman and ^{13}C NMR spectroscopy. The results show the formation of a hybrid polymer with carbon and silicon in the macromolecule chain and the transition metal cation arrested within this polymeric chain. The nanocomposites are formed during the controlled polymeric precursor pyrolysis. The reduction of the metal cation is promoted by the CO/CO_2 atmosphere resulting from the pyrolysis of the organic material. Microstructural characterization, performed by TEM and X-ray diffraction (XRD), showed that the nanocomposites are formed by metal nanoparticles embedded in a amorphous matrix formed by SiO_2 and carbon. In the SiO_2 :Fe system, Fe_3C was also detected by XRD.

H7.35

SELF-ASSEMBLED ORGANIC/INORGANIC NANOCOMPOSITES. Byron McCaughy, Donghai Wang, Eric Hampsey, Xianglin Ji, and Yunfeng Lu, Chemical Engineering Department, Tulane University, New Orleans, LA.

Nanostructures with critical dimensions less than 100 nm endow materials with unique and often superior mechanical, electronic, magnetic and optical properties, which can open a new avenue to numerous advanced applications. The method of self-assembly that spontaneously assembles and organizes various building blocks into hierarchical structures via non-covalent interactions has emerged as one of the most promising techniques to the efficient fabrication of nanostructured materials. Here we report the formation of organic/inorganic nanocomposites using the methods of sol-gel process and surfactant self-assembly. This method relies on spontaneous cooperative-assembly of silicate and surfactant molecules that spatially organizes the organic and inorganic components into two- or three-dimensional ordered nanostructures. Highly ordered (e.g., hexagonal, cubic, or lamellar mesostructured) silica/polymer nanocomposites containing conjugated areneethynylene polymers, ethynylene polymers, or diacetylene polymers has been fabricated using this method. The properties of these nanocomposites have been studied using different techniques and the results indicate that the nanostructure may endow these nanocomposites unique properties.

H7.36

NANOPARTICLE INKS FOR DIRECTED ASSEMBLY OF 3-D PERIODIC STRUCTURES. Qi Li, Gregory Gratson, and Jennifer A. Lewis, University of Illinois, Urbana, IL; James Smay, Oklahoma State University, Stillwater, OK.

Nanoparticle assembly of 3-D periodic structures requires control over, and, hence, a fundamental understanding of interparticle forces, phase behavior, and structure evolution during fabrication. This talk focuses on the fabrication of mesoscale periodic structures via directed assembly of concentrated nanoparticle inks. Concentrated nanoparticle gel-based inks with tailored viscoelastic properties were designed to produce 3-D structures with self-supporting features. The inks were robotically deposited in a layer-by-layer sequence to directly write the desired 3-D pattern. 3-D periodic structures with spanning features that vary between ~ 100 nm and 1 mm were created from functional nanoparticle inks consisting of ferroelectric barium titanate particles ($D \sim 60$ nm).

H7.37

WET PROCESS MOLECULAR PLANTING IN A SPECIFIC SITE OF SILICON WITH Si-C COVALENT BONDS. Hirokazu Tada, Masato Ara, Shoji Tanaka, Institute for Molecular Science, Okazaki, JAPAN.

Alkyl monolayers anchored covalently on silicon were prepared through the reaction between 1-alkenes and hydrogen-terminated silicon (111). The 2D-patterning of the surface was done by local oxidation with an atomic force microscope (AFM) and 3D-molecular assemblies were fabricated by molecular planting in a specific site of the surface. The surfaces were anodized with a contact-mode AFM by applying a positive bias voltage to the surface with respect to the platinum-coated cantilever under ambient conditions, which resulted

in nanometer-scale oxidation of surfaces. The threshold voltage was 5V for anodization of silicon covered with a dodecyl monolayer, which was lower than that for siloxane monolayers examined so far. The alkyl monolayers showed high resistance against chemical etching and air-oxidation. The anodized areas were etched and terminated with hydrogen atoms by NH_4F solution, in which we could plant various molecules having $\text{C}=\text{C}$ bonds. We planted arylamine molecules to which organic dyes such as fluorescein and porphyrin were anchored through amido-couplings. The intensity of luminescence was varied depending on dopant concentration of substrates. Luminescence was very weak on highly-doped silicon possibly due to effective energy transfer from dyes to substrates. The interaction between molecules and substrates will be discussed by using the well-controlled molecular semiconductor hybrid systems.

H7.38

DENDRIMER MEDIATED 'BRICKS AND MORTAR' SELF-ASSEMBLY OF NANOPARTICLES. Benjamin L. Frankamp, Andrew K. Boal, Vincent M. Rotello, University of Massachusetts, Department of Chemistry, Amherst, MA.

Control of particle-particle spacing is a key determinant of optical, electronic, and magnetic properties of nanocomposite materials. We have used poly(amidoamine) (PAMAM) dendrimers to assemble carboxylic acid-functionalized mixed monolayer protected clusters (MMPCs) through acid/base chemistry between particle and polymer. IR spectroscopy and selective dendrimer staining, observed by Transmission Electron Microscopy (TEM), establish that the PAMAM dendrimers are the mortar in the assembly and act to space the MMPCs in the resulting aggregates. Small angle X-ray scattering (SAXS) was then used to establish average interparticle distances; five generations of PAMAM dendrimer (0, 1, 2, 4, 6) were investigated and monotonic increase in interparticle spacing from 4.1 nm to 6.1 nm was observed. Initial studies involving the application of this methodology to control the magnetic properties of γ -iron oxide nanoparticles have been completed. γ -Iron oxide nanoparticles (6.5 nm in diameter) have been assembled with PAMAM dendrimers generations 2.5, 4.5, and 6.5. The resulting aggregates were characterized with SAXS and magnetization obtained on a superconducting quantum interference device (SQUID). An observed correlation between the blocking temperature (T_b) and the average interparticle spacing suggests that our methodology could be used to tailor the magnetic profile of the nanoparticles.

H7.39

SELF ASSEMBLY OF MAGNETIC AND SEMICONDUCTING NANOPARTICLES: BUILDING BLOCKS FOR NANOTECHNOLOGY. Franz Redl, Stephen O'Brien, Ming Yin, Stephanie Grancharov, Columbia University, Materials Science and Engineering, Dept. of Applied Physics, New York, NY; Christopher B. Murray, K.-S. Cho, Glenn Held, IBM T.J. Watson Research Center, Yorktown Heights, NY.

One of the central challenges nanotechnology seeks to address is the ability of the materials components to self-assemble into ordered arrays that will have function and utility. Physical, chemical, optical, magnetic or electronic properties of nanostructured materials can be tuned by adjusting size, shape and surface-modification. In order to take advantage of nanoscale materials we seek to control their arrangement into utilizable dimensions. A nanoscale approach to this issue combines the advantage of miscibility of different materials by applying solution cast methods with close vicinity in the resulting dense material (although direct contact between particles is avoided by the surfactant). We describe the formation of a bimodal three-dimensional nanocrystal superlattice of magnetic iron oxide nanoparticles forming a framework of superparamagnetic spheres and semiconducting lead selenide nanoparticles. The crystals were obtained by self-assembly of the materials during co-crystallization from solution. We are exploring routes to novel synthesis of magnetic and semiconducting nanoparticles based on new materials and new inorganic chemical techniques. Iron oxide particles constitute a diverse class of materials displaying a range of optical, magnetic and catalytic properties. Ferrimagnetic iron oxides have applications in magnetic storage, high frequency transformers and RF and microwave components. In addition to electronic applications the stability and bio-compatibility of the iron oxides are making them leading candidates for drug delivery, diagnostic and medical imaging applications. We have worked to develop synthetic routes for the preparation of highly crystalline monodisperse nanoparticles of γ - Fe_2O_3 and are pursuing similar techniques for the other iron oxides. Fe_3O_4 (magnetite) and γ - Fe_2O_3 are both ferrimagnetic making them interesting to models to explore magnetic stability and the superparamagnetism in ferrimagnetic systems.

H7.40

SYNTHESIS, STRUCTURE, AND MAGNETIC PROPERTIES OF $\text{Fe}_x\text{Pt}_{95-x}\text{Cu}_{15}$ NANOCOMPOSITE PARTICLES. Xiang-Cheng Sun,

D.E. Nikles, S.S. Kang, J.W. Harrell, Center for Materials for Information Technology, The University of Alabama, Tuscaloosa, AL; Z.R. Dai, J. Li, Z.L. Wang, School of Materials Science and Engineering, Georgia Institute of Technology, Atlanta, GA.

$\text{Fe}_{x}\text{Pt}_{85-x}\text{Cu}_{15}$ nanoparticles were synthesized by simultaneous chemical reduction of platinum acetylacetonate and copper bis (2,2,6,6-tetramethyl-3,5-heptanedionate) and thermal decomposition of iron pentacarbonyl. The relative amounts of iron, platinum and copper in the particles depended on the amount of iron, platinum and copper charged to the reaction. As-made the particles possessed a disordered face-centered cubic (FCC) lattice with an average diameter of 3.5 nm and were superparamagnetic. These particles were well dispersed in hydrocarbon solvents and self-assembled into granular film when deposited onto carbon coated Cu TEM grids or single crystal Si(100) substrates. After ex-situ annealing from 500°C to 700°C under an Ar+H₂ atmosphere, the particles transformed into the tetragonal phase (L1₀, FCT). The coercivity (H_C) of the annealed film strongly depended on the composition and the ex-situ annealing temperature. The H_C first increased with increasing annealing temperature up to 550°C. And then the H_C decreased after annealing at temperature higher than 550°C. It suggested that higher annealed temperature led to exchange coupling and incoherent magnetization reversal, which resulted in the H_C dropped significantly. XRD patterns indicated that even the chemical ordering improved with annealing at higher temperatures (> 550°C), a ternary FePtCu alloy phase was found on the annealed surface of granular thin films. Therefore it is also reasonable that effective volume of L1₀ phase decreased due to surface magnetically soft phase on annealed sample surface. The above results were very different with sputtered FePtCu thin films.

H7.41
MOLECULAR-DYNAMICS STUDY OF THE MECHANICAL PROPERTIES OF METAL NANOWIRES. T. Nakajima, K. Shintani, Univ of Electro-Comm, Dept of ME & Intelligent Sys, Tokyo, JAPAN.

Observations of single arrays of metallic atoms in scanning tunneling microscopy studies have provoked prosperity of investigations of nanowires. Nanowires have some unique properties at their nanoscale such as quantized conductance and long bond-length which are not observed for materials at the larger dimensions. It can also be expected that the mechanical behaviors of nanowires under external forces, e.g. their stress-strain relationship and plasticity, are different from the ones of the macroscopic materials. In this study, molecular-dynamics simulation is employed to study deformation of metal nanowires under tensile strain. The interaction forces between metallic atoms are calculated by using the embedded-atom method potential. Before a tensile process begins, a model nanowire is equilibrated at a specified temperature. A few layers at one end of the nanowire are kept fixed. A few layers at the opposite end are forced to be displaced until the nanowire breaks. Its deformation is observed throughout the tensile process. How the structural anisotropy of nanowires affects their deformation behaviors and mechanical properties is investigated.

H7.42
EFFECTIVE MEDIUM CALCULATIONS OF THE ELECTROMAGNETIC BEHAVIOR OF SINGLE WALLED CARBON NANOTUBE COMPOSITES. John W. Schultz, Georgia Tech Research Institute, Atlanta, GA.

The high aspect ratio and unique conductive behavior of carbon nanotubes provide opportunities for new composite materials with useful RF and microwave properties. Coating or filling carbon nanotubes with insulating or metallic materials can provide further enhancements to their electromagnetic properties. Some applications in EMI and telecommunications require lightweight conductive materials while other applications call for low loss substrate materials with high dielectric constants. Dielectric properties of single walled carbon nanotube assemblies were calculated with an effective medium approximation at frequencies from 200 MHz to 200 GHz. The model treats the carbon nanotubes as layered cylinders, each with a core, a graphene layer and an outer layer, to investigate the dielectric properties of coated and filled nanotubes. The graphene and metal layer properties were modeled with a Drude approximation based on literature data. A generalized Bruggeman model was then used to determine the macroscopic behavior of the modified carbon nanotubes in a composite structure as a function of volume fraction, frequency, and aspect ratio. The depolarization factors in this model were scaled by the normalized effective permittivity to better account for percolation behavior. The model showed a wide variety of frequency dependent dielectric properties. Uncoated tubes were calculated to form highly conductive materials at volume fractions of just a few percent and metal-coated tubes enhanced the conductivity by an order of magnitude. Calculations of nanotubes with insulating coatings showed that high dielectric constants with moderate to low

dielectric loss were possible. For example, a permittivity of over 150 with a loss tangent of less than 0.1 was calculated at 1 GHz with a 10 vol% composite of nanotubes that were coated with a 5 nm thick insulating sheath.

H7.43
IONIC COLLOIDAL CRYSTALS PRODUCED VIA CONTROLLED HETEROCOAGULATION. Garry R. Maskaly, R. Edwin Garcia, W. Craig Carter, Yet-Ming Chiang, Massachusetts Institute of Technology, Dept of Materials Science, Cambridge, MA.

Ionic colloidal crystals (ICCs) are here defined as ordered multicomponent colloids formed through heterocoagulation (electrostatic interactions). The conditions under which ICCs are stable have been analyzed. A model is presented in which two dimensionless parameters are found to fully characterize an ICC system. We calculate the Madelung constant of several ICC structures as a function of these two parameters, and discuss the parallels between the ICC Madelung constants and those for classical ionic crystals. Experimentally accessible regions of surface charge, salt concentration, and temperature where ionic crystallization should be possible are identified.

H7.44
AB INITIO STUDY OF THE ANODIZATION PROCESS OF CRYSTALLINE SILICON IN THE PRESENCE OF HF. Thompson Le Blanc, Daniel Melendez, Ivan Cao-Berg, Javier Avalos, Univ. Metropolitana, San Juan, PR.

Structures of nanometric porous silicon surface will be studied Ab Initio using MP2 and B3LYP basis sets, procedures which efficiently samples minima on a potential energy surface. This Scholastic procedure will try to model anodization process where the surface of the crystalline silicon becomes porous on the presence of HF. The most stable structures will be presented. It is shown so far that using the basis-set as described in the investigation, there was no change in the electronic density. In the future we will be using different basis-sets and smaller.

SESSION H8: FABRICATION AND PROPERTIES OF 3D-ORDERED NANOSTRUCTURES
Chairs: David P. Taylor and Koji Ikuta
Thursday Morning, December 5, 2002
Room 309 (Hynes)

8:30 AM *H8.1
THREE-DIMENSIONAL NANOSTRUCTURE FABRICATION BY FOCUSED-ION-BEAM CHEMICAL VAPOR DEPOSITION. Shinji Matsui, Himeji Institute of Technology, Kamigori, Ako, Hyogo, JAPAN.

Two-dimensional nanostructure fabrication using electron-beam (EB) and focused-ion-beam (FIB) has been achieved and applied to make various nanostructure devices. Ten-nm structures are able to be formed by using a commercial available EB or FIB system with 5 nm beam diameter and high-resolution resist. In this way, it is considered that the technique of two-dimensional nanostructure fabrication has been established. On the other hand, three-dimensional nanostructure fabrication has been also studied using both EB and FIB induced deposition (CVD). The deposition rate of FIB-CVD is much higher than that of EB-CVD due to factors such as the difference of mass between electron and ion. Furthermore, FIB-CVD has an advantage over EB-CVD in that it is more easily to make a complicated 3-dimensional nanostructures. Because, a smaller penetration-depth of ion compared to electron allows to make a complicated 3-dimensional nanostructures. For example, when we make a coil nanostructure with 100 nm linewidth, electrons with 10-50 keV pass the ring of coil and reach on the substrate because of large electron-range (over a few 10 nm), so it is very difficult to make a coil nanostructure by EB-CVD. On the other hand, as ion range is less than a few 10 nm, ions stop inside the ring. This paper presents a complicated 3-dimensional nanostructure fabrication using FIB-CVD. A carbon-coil with 600 nm diameter and 80 nm linewidth, which was made by 30 kV Ga⁺ FIB with carbon containing source (phenanthrene) gas. This demonstrated that FIB-CVD is very useful to make a complicated 3-dimensional structures. Moreover, we report an evaluation of the Young modulus of such amorphous carbon pillars by measuring the resonant frequency of pillars. The spontaneous vibration of pillars was detected in SEM electron beams, and the resonant characteristics were analyzed through the signals of a secondary electron detector.

9:00 AM H8.2
FORMATION OF 3-Dimensionally Orientated NANO-SIZED CRYSTALS IN AN AMORPHOUS ALLOY UNDER ION BEAM IRRADIATION. Ryuichi Tarumi, Takuya Kamikawa,

Kazuki Takashima and Yakichi Higo, Tokyo Inst of Technology, Tokyo, JAPAN.

Nano-sized crystals (NCs) have been intensively investigated in the past decade because of their excellent properties. Several methods have been proposed to obtain NCs, such as recrystallization following severe plastic deformation, epitaxial growth, etc. Using these methods, however, it is difficult to obtain the grain size of NCs less than 10 nm. One of the attractive ways to control the structure of materials in the order of several nano-meters is ion beam irradiation. Up to now, most ion beam irradiation studies have been performed on crystalline materials, with little on amorphous alloys. Amorphous alloys are in a thermally nonequilibrium state, so that crystallization may occur under ion beam irradiation, but details have not been clarified. In this study, we have examined the structural change of an amorphous alloy under ion beam irradiation. The material used in this study was a Ni-11.5wt%P amorphous alloy. Specimens were fabricated into a circular disk with a diameter of 3 mm. Prior to ion beam irradiation, two types of irradiation beams, that were focused and unfocused, were used with ion sources of Ga and Ar respectively. Transmission electron microscopy observation of the area revealed the formation of NCs with grain sizes of approximately 5 nm in the amorphous matrix with both ion sources. The crystalline structure of NCs was determined as a fcc from electron diffraction analysis. Furthermore, the NCs formed had a crystallographic orientation relationship with the ion beam direction, that is, a (111) of NCs was parallel to the irradiated surface. NCs had a specific orientation relationship with each other in the irradiated plane. These results suggest that ion beam irradiation techniques have the possibility to form three-dimensionally orientated NCs in amorphous alloys. The mechanism of formation of crystallographically orientated NCs under ion beam irradiation will be discussed.

9:15 AM H8.3

NANOMETER-SCALE PATTERN TRANSFER BY ION IMPLANTATION AND SELECTIVE CHEMICAL ETCHING. Naomi Matsuura, Xiang-Yang Mei, P. Morales, Harry E. Ruda, University of Toronto, Dept of Materials Science and Engineering, Toronto, CANADA; Todd W. Simpson, Chris P. McNorgan, Ian V. Mitchell, University of Western Ontario, Dept. of Physics & Astronomy, London, CANADA.

Conventional, broad-area, ion implantation through 3-d masks is combined with selective wet chemical etching to create a pattern of 3-d features, periodic in 2-d. Two examples are discussed. In the first, a self-assembled array of silica spheres is used as an implant mask. The thickness variation due to the geometry of the spheres provides variable implantation depth in a periodic fashion. The ion beam amorphized regions of the substrate are then removed by selective chemical etching to achieve 3d patterning. In the second example, self-assembled, nanometer-sized hole arrays are produced by electrochemical etching in alumina. The porous alumina films are then used as an implant mask to produce a periodic array of high aspect ratio, 40nm diameter holes on 100nm spacing in a single crystal substrate. We discuss the directions in which this type of lithography might be taken.

9:30 AM H8.4

3D MICRO- AND NANO-FABRICATION OF METAL NANOPARTICLE PATTERNS AND CONDUCTIVE METAL STRUCTURES VIA ONE- AND TWO-PHOTON INDUCED LITHOGRAPHIC AND HOLOGRAPHIC METHODS.

Francesco Stellacci, Christina A. Bauer, Wim Wenseleers, Timo Meyer-Friedrichsen, Valérie Alain, Stephen M. Kuebler, Seth R. Marder, Joseph W. Perry, Department of Chemistry, The University of Arizona, Tucson, AZ.

The photochemical generation of metal nanoparticles and metal structures in a solid matrix has recently attracted attention.^[1,2] We have shown^[3] that the use of a photoreducing dye that was designed to have a large two-photon cross-section and that was dissolved in a polymer matrix with a soluble silver salt (AgBF₄) allows for the photochemical generation of isolated silver nanoparticles. When the excitation is generated by use of interfering laser beams, the resulting refractive index contrast is sufficient for the one-step formation of very stable holographic images. The use of two-photon irradiation allows for the formation of 3D nanoparticle-containing patterns in a polymer matrix. We show that the enhanced fluorescence and/or the refractive index contrast, generated following exposure, can be used for 3D data storage. In order to obtain continuous metal features in a polymer matrix, pre-nucleated metal crystals have been dissolved in the matrix. Tailor-made ligand-coated metallic nanoparticles can be readily synthesized, and can be made highly soluble in complex composite materials or can be self-assembled and thermally annealed into ordered films. We have demonstrated^[3] that, in the presence of suitable reducing dyes and metal salts, it is possible to induce the growth of metal nanoparticles either under optical excitation or under

electron-beam irradiation. We show further that it is possible to obtain continuous and conductive metal structures using optical excitation and that, with two-photon excitation, 3D self-standing structures can be fabricated and characterized. Silver, copper, and gold microstructures will be presented. Finally, we will describe nanoparticles functionalized with covalently bonded dyes: these particles can grow when the dyes are irradiated with light or electron-beams. 1. P.W. Wu, et al., Adv. Mat. 12, 1438 (2000). 2. T. Deng, et al., An. Chem. 72, 645 (2000). 3. F. Stellacci, et al., Adv. Mat. 14, 194 (2002).

9:45 AM H8.5

FABRICATION OF PERFORATED FILM NANOSTRUCTURES. A.L. Elias, K.D. Harris and M.J. Brett, Dept of Electrical and Computer Engineering, Univ of Alberta, Edmonton, CANADA.

We have demonstrated the fabrication of perforated thin films (PTFs), comprised of thin coatings perforated with unusual pore shapes such as helices or chevrons. PTFs are fabricated using a template of nanosprings or nanochevrons of diameter nominally 200 nm produced using the Glancing Angle Deposition (GLAD) technique. GLAD utilizes a combination of extreme oblique incidence physical vapour deposition with controlled substrate motion to engineer specific porous nanostructures. PTFs have been produced by filling template helical GLAD films with various substances, etching back the coating to reveal the tips of the helices, and etch removal of the helical template. We will report a range of novel nanostructured materials fabricated using the PTF technique, including ordered periodic arrays of helical perforations, utilizing a template of arrayed nanosprings. We are developing a process for fabricating metal PTFs, in which electroplating is used to fill the original template. We will also report a replica process, using PTFs as a template, from which nanohelices can be fashioned in materials that cannot otherwise be used in the GLAD process, such as polymers. Results of characterization of these structures will be presented, including structural and optical analysis. Preliminary results show that helical PTFs have a strong chiral optical activity.

10:30 AM *H8.6

NANOTECHNICS: FABRICATION OF INORGANIC TRANSISTORS AND MICRO-ELECTRO-MECHANICAL SYSTEMS FROM NANOPARTICLE BUILDING BLOCKS.

Joseph Jacobson, Eric Wilhelm, Colin Bulthaupt and Brent Ridley, The MIT Media Lab Center for Bits and Atoms, Massachusetts Institute of Technology Cambridge, MA.

Recently the authors have developed an approach termed Nanotectonics for the all-printed fabrication of both inorganic logic elements (Science 286 (5440) 746) and micro-electro-mechanical systems (MEMS) using nanoparticle building blocks. Using this approach the authors have fabricated both inorganic transistors, including passive components such as resistors, capacitors, inductors and vias necessary for universal logic, as well as MEMS devices. We report on recent results using this approach.

11:00 AM H8.7

ASSEMBLY OF SEMICONDUCTOR AND MAGNETIC NANOCRYSTALS INTO BINARY NANOCRYSTAL SUPERLATTICES. F.X. Redl, IBM Corp; K.S. Cho, IBM Corp and University of New Orleans; C.B. Murray, IBM Corp, Yorktown Heights, NY.

We present the co-assembly monodisperse Fe₂O₃ nanocrystals and PbSe nanocrystals into a 3 dimensional nanocrystals superlattice with and AB13 intermetallic structure. Methods for direct the assembly of the nanocrystals will be discussed. The systematic to systematic structural characterization of these binary superlattices (colloidal crystals) will also be presented. These binary nanocrystal superlattices are a new class of magneto-optic composites.

11:15 AM H8.8

SYNTHESES OF COMPLEX-SHAPED, 3D, SELF-ASSEMBLED NANOPARTICLE STRUCTURES WITH TAILORED CHEMISTRIES BY THE BASIC PROCESS. Frank Zalar, Matthew Dickerson, Raymond Unocic, Ken Sandhage, Dept of Materials Science and Engineering, Ohio State Univ, Columbus, OH; Rajesh Naik, Gunjan Agarwal, Morley Stone, Materials and Manufacturing Directorate, Air Force Research Laboratory, Wright-Patterson AFB, OH.

A novel approach for fabricating large numbers of complex-shaped, three-dimensional (3-D) nanoparticle structures with tailored chemistries is presented: the Bioclastic and Shape-preserving Inorganic Conversion (BaSIC) process[†]. A "bioclastic" structure is a mineralized object with a shape that has been attained through the action of a living organism. Among the most striking bioclastic structures are the frustules of diatoms. Diatoms are single-celled algae

that are ubiquitous to aquatic (marine and freshwater) environments. Diatoms form intricate 3-D frustules (microshells) comprised of assemblies of silica nanoparticles. The number of extant diatom species is $\approx 10^4$ to 10^5 . Each species of diatom forms a frustule with a unique shape and with fine, distinctive features (e.g., pores, ridges, protuberances). Continued reproduction of a given diatom can yield large numbers (e.g., billions) of daughter diatoms with similarly-shaped frustules. Such massively parallel 3-D self-assembly of complex-shaped nanoparticle structures can be highly attractive for nanotechnological applications. However, the range of potential applications is limited by the silica-based chemistry of diatom frustules. The compositional limitations of bioclastic structures can be overcome in the BaSIC process through the use of shape-preserving fluid/solid reactions. This process has been demonstrated via the reactive conversion of two types of biologically-derived preforms: i) naturally-occurring diatom frustules (e.g., capsule-shaped *Aulacoseira*, disk-shaped *Cyclotella*), and ii) biocatalyzed multifilamentary silica structures. The latter structures were produced through the use of silaffins (biocatalysts derived from diatoms). These preforms were converted into alkaline earth-bearing oxides (MgO-bearing or CaO-bearing) by exposure to elemental gases (Mg(g) or Ca(g)) at $\geq 750^\circ\text{C}$. Electron microscopy (SEM, TEM) has revealed that the preform shapes and fine features were preserved after conversion. Conversion reactions to other ceramics are also under investigation. Such shape-preserving chemical conversion, coupled with future genetic tailoring, could ultimately yield a variety of Genetically-Engineered Meso/nanodevices (GEMs). [†]U.S. Patent Application.

11:30 AM H8.9

NANOPARTICLE RIBBONS: A METHOD FOR FABRICATING COMPLEX 3-D ELECTRONIC CIRCUITS. Venugopal Santhanam, Ronald P. Andres, Purdue Univ, School of Chemical Engineering, West Lafayette, IN; Jaewon Choi, David B. Janes, Purdue Univ, School of Electrical and Computer Engineering, West Lafayette, IN; Stephen W. Howell, Ronald Reifenberger, Purdue Univ, Department of Physics, West Lafayette, IN; Scott E. Burns, Clifford P. Kubiak, University of California, San Diego, Department of Chemistry and Biochemistry, La Jolla, CA.

The huge size mismatch between typical organic molecules and lithographically defined structures is a critical problem hindering implementation of "molecular electronics". One solution to this problem is to self-assemble circuits using nanometer-scale gold particles as conducting nodes physically linked and electrically coupled by organic molecules that have terminal thiol or isonitrile groups (e.g. Science 273, 1690 (1996)). Researchers have been able to fabricate small monolayer arrays of such molecularly linked nanoparticles, but in order to construct functional devices and circuits, methods must be developed for fabricating lines or ribbons of linked nanoparticles and for assembling layers of these ribbons one on top of the other with selected organic molecules forming the interconnections between each layer. We describe a suite of techniques for construction of such 3-D nanoengineered assemblies: 1) a self-assembly method of forming a uniform, close-packed monolayer of alkanethiol encapsulated gold nanoparticles spanning centimeters; 2) a soft lithographic method for transferring nanoparticle ribbons selected from this ordered film to a solid substrate; 3) a method for replacing the alkanethiol molecules on the particles with conjugated dithiol molecules, which lower the lateral electrical resistance of the ribbons by three orders of magnitude; 4) and finally a method for layering nanoparticle ribbons one on top of the other and forming defined molecular junctions between them. We characterize these 3-D nanoengineered assemblies using Transmission Electron Microscope, and Kelvin Probe Microscope studies along with UV-Vis, and I-V measurements.

11:45 AM H8.10

3D NANOENGINEERING OF METAL OXIDES AND OXYHYDROXIDES FROM AQUEOUS SOLUTION. Lionel Vayssieres, Arumugam Manthiram, Texas Materials Institute, The University of Texas at Austin, Austin, TX.

The ability to design anisotropic nanoparticles with tailored aspect ratio and to order them into large 3D array is an important challenge, scientists have to face to create smart and functionalized nanomaterials. Our approach to control the size and shape of nanoparticles as well as the overall texture of nanomaterial thin films is to tune their direct aqueous hydrolysis-condensation growth onto substrates by monitoring the interfacial thermodynamics of nanocrystals as well as their kinetics of heteronucleation. This is achieved by minimizing the surface energy at the Water/Oxide interface according to a general quantitative model based on Gibbs adsorption equation. Indeed, growing materials at low interfacial tension, i.e. at thermodynamically stable conditions, allows to control experimentally the extension and rate of the nucleation stage and therefore different size, shape and orientations can be generated onto

various substrates. Consequently, the design of novel devices with tailored and engineered three-dimensional architecture can be obtained without template or surfactant. Such ideas will be demonstrated and illustrated on the design of nanorods and nanowires of zinc oxide, iron oxide and manganese oxide materials, their growth as 3D arrays with parallel and perpendicular orientation with respect to the substrate as well as the characterization of their electronic structure and optoelectronic properties.

SESSION H9: APPLICATIONS OF FUNCTIONAL NANOSTRUCTURES

Chairs: Lhadi Merhari and David P. Taylor
Thursday Afternoon, December 5, 2002
Room 309 (Hynes)

1:30 PM *H9.1

ADVANCED CHEMICAL GAS SENSORS FOR OUTDOOR AIR QUALITY MONITORING. Marie-Isabelle Baraton, UMR CNRS 6638, Faculty of Sciences, Limoges, FRANCE.

The popular Taguchi-type SnO₂-based sensors are often used as low-cost alarm devices to monitor the indoor air quality. However they are not suitable for outdoor air quality monitoring due to their insufficient sensitivity to pollutant gases like CO, NO, NO₂ and O₃ at the sub-ppm level. I will review the results of two major research programs we undertook to optimize chemical gas sensors based on metal oxide semiconductors. Four major topics will be treated here: 1- why and how the use of nanopowders in the fabrication of screen-printed gas sensors leads to increased sensitivity. 2- how the printing of the sensitive layer on the alumina tiles using a simple mechanical layer-by-layer technique leads to further increase of the gas sensitivity, thus showing a beneficial effect of a 3D assembly of nanoparticles. 3- why the surface chemistry of nanoparticles is critical and must be tailored to optimize chemical sensors. 4- which of SnO₂, In₂O₃ and WO₃ nanopowders obtained by laser evaporation gives the best sensitivity to CO, NO_x and O₃ in presence of humidity. The prototype devices which could detect O₃ and NO_x concentrations down to 20 ppb and 50 ppb respectively, and CO concentrations down to 3ppm in air were characterized by various methods including XRD, TEM, FTIR, and electrical measurements. The SMOGLess and INTAIRNET projects were financially supported by the European Community (contracts numbers BRPR-CT95-0002, and IST-12615).

2:00 PM H9.2

CHARACTERIZATION OF NANOASSEMBLED TIN-OXIDE NANOPARTICLES FOR FABRICATION OF A HIGH SELECTIVITY MICRO GAS SENSOR. R.C. Ghan, Y. Lvov, R.S. Besser, Institute for Micromanufacturing and Chemical Engineering, Louisiana Tech University, Ruston, LA.

We are investigating properties of SnO₂ nanoparticles deposited using a novel Layer-by-Layer (LbL) technique in order to develop a high selectivity, nanostructured, semiconductor micro gas sensor. While SnO₂ for gas sensing is not new, the advantages of the LbL process give promise for a new class of precision sensing layers nanoengineered from readily available nanoparticle building blocks. As presented in the MRS Fall Meeting, Boston, 2001, we have achieved precision SnO₂ nanoparticle deposition on QCM resonators using the electrostatic self-assembly technique [1]. Besides SnO₂ films, films of SiO₂/SnO₂ were alternately assembled with a view to investigating doping effects. SEM characterizations of as-deposited films show that the SnO₂ nanoparticle thin films are grown uniformly across the substrate. The size range for the nanoparticles is 3-5 nm. Electrical characterization of newly prepared macro-scale prototypes reveals linear current-voltage characteristics indicating ohmic behavior. An issue in the use of the LbL process is the presence in the film of residual organic remnants from the growth process. Calcination experiments show significant residue, even after 500°C. This is a matter of concern as the use of higher temperatures begins to diminish the basic advantages of the LbL process over conventional ceramics processes. We will present the results of these studies, and others for removing residual polymer components. We will also show the results of an alternative approach for preserving the electrical activity of the tin oxide nanoparticles while maintaining lower processing temperatures. References: [1] R.C. Ghan, Y. Lvov, R.S. Besser, "Characterization of Self-Assembled Tin-Oxide Films for High Sensitivity Micro-Gas Sensors," MRS Proceedings, Materials Research Society, College Park, MD, 2001.

2:15 PM *H9.3

NANOMECHANICAL SYSTEMS. H.G. Craighead, Applied and Engineering Physics, Cornell University, Ithaca, NY.

We have created mechanical devices, using a variety of materials, that we have been studying as sensors and other applications. In most cases the motion of these devices was detected and in some cases

actuated by the application of light. Spatially varying mechanical driving of micromechanical structures was also demonstrated using a scanning probe tip for actuation and an electron beam to detect motion. Sensor applications include immunospecific detection of single bacterial cells and chemical monolayers. Parametric amplification of mechanical motion was demonstrated in a variety of device configurations, with optical and electrodynamic drive. High-resolution lithographic processes have been used to create similar resonant mechanical systems with dimensions down to tens of nanometers. The smaller devices are also more susceptible to surface related mechanical loss mechanisms, which we have begun to study. Related nanofabrication approaches have also been used to create nanostructures for the mechanical manipulation and sorting of molecules by mechanical and physical properties in a variety of fluid containing system configurations. Mechanical confinement of fluid systems has also been used to enable optical detection and analysis of individual biomolecules.

2:45 PM H9.4

OPTICALLY DRIVEN MICROMANIPULATION TOOLS

FABRICATED BY TWO-PHOTON MICROSTEREO-LITHOGRAPHY. Shoji Maruo, Koji Ikuta and Hayato Korogi, Department of Micro System Engineering, School of Engineering, Nagoya University, Aichi, JAPAN.

Manipulation techniques at micro and nanometer length scale are crucial for advance in biotechnology as well as nanoscale science and technology. Recently several types of nanomanipulators such as carbon nanotube nanotweezers and micromachined nanotweezers have been developed for grabbing or probing micro/nano scale objects. However, since these tweezers are based on electrostatic force, they are not ideal for aqueous solution work such as manipulation of cells, microbes and single molecules. In this paper, we report optically driven micromanipulators suitable for biological applications that require work in aqueous solution. Our manipulators were fabricated by using two-photon microstereolithography [1, 2]. These micromanipulators are driven by optical trapping based on radiation pressure from a tightly focused laser beam. Since optical trapping enables remote driving of movable micromechanisms in biological fluid environments, the micromanipulators are well suited for the application in bionanotechnology. The main advantages of our optically driven manipulators are as follows: 1) Remote drive suitable for aqueous solution work, 2) Femtonewton force control, and 3) Easy integration into micro total analysis systems. We fabricated micromanipulators whose arms is 8.7 μm long and 1.7 μm wide. By trapping and swinging a manipulator arm with a focused laser beam, the micromanipulators were successfully opened and shut in a liquid. In addition, we succeeded to control the torque of the manipulators by adjusting the position trapped by the laser beam along the length of the arm. The range of the torque was on the order of 10^{-19} Nm. Finally, we developed microtweezers and microneedle with probe tips of diameter 250 nm. These manipulators were also driven in a liquid. Such optically driven micro/nano manipulators are promising tools for bionanotechnology and micro total analysis system.

[1] S. Maruo, et al., Proc. of MEMS 2001, p.594. [2] S. Maruo, et al., Opt. Lett. vol. 22, p.132 (1997).

3:30 PM H9.5

BIOLOGY DOES IT DIFFERENTLY. HOW CAN WE HARNESS ITS ADVANTAGES? Daniel E. Morse, Jan Sumerel, Wenjun Yang, James Weaver, Germaine Fu, Timothy Deming, Bradley F. Chmelka, Galen D. Stucky and Paul K. Hansma, University of California at Santa Barbara, Biomolecular Science and Engineering and Materials Research Laboratory, Santa Barbara, CA.

Biological systems fabricate 3-dimensional nanostructured composites by mechanisms that are both more precise than, and fundamentally different from, those of current technologies. Two examples are discussed. (1) Whereas multi-layer spin-coating, dipping or stenciled vapor deposition strategies are used in current manufacturing technologies to produce multi-layered structures for microelectronics, the biological mechanism underlying formation of the microlaminate mineral-organic composite forming the nacre of pearls and seashells is fundamentally different. Microlaminate nacre is organized over macroscopic dimensions by continuous growth of atomically coherent aragonite crystals propagating from one layer to the next through nanopores in a multilayered network of sheets composed of a fabric of proteins and polysaccharides. Stochastic spacing of the stencil-like nanopores in these interlamellar sheets determines the lateral offset between successive microlaminae, thus generating the interdigitating brickwork of crystalline plates that contributes to enhanced fracture toughness. While this mechanism generates the hierarchically organized multilaminate pattern, families of small proteins interact stereospecifically with the growing crystals to control their polymorph, atomic lattice orientation and morphology. (2) The intricate structures of silica produced biologically in sponges in diatoms similarly reflect the continual operation of multiple mechanisms

operating contemporaneously at different length scales. In sponges, for example, the formation and deposition of silica is catalyzed and nanostructurally directed (from the "bottom up", in contrast to differential lithographic and etching technologies) by a unique family of enzymes that simultaneously provide the catalytic centers for the formation of silica while at the same time providing the templates for its deposition. Higher-order structural control is thought to result from phase-separation operating in conjunction with molding by the surrounding lipid membranes. Higher order branching of silica spicules in sponges reflects the controlled branching of the structure-directing proteins on which the silica is deposited, but understanding the regulation of this branching at the protein (catalytic template) level presents a significant challenge. Progress in biomimetic adaptation of these mechanisms - including methods now in use by specialized sectors of the semiconductor industry - will be discussed.

4:00 PM H9.6

FABRICATION OF 3-D BIOACTIVE STRUCTURES.

Kenneth E. Gonsalves, Dept. of Chemistry & C.C. Cameron, Applied Research Center, Univ. of North Carolina, Charlotte, NC; Wei He, Dept. of Chemistry, Univ. of Connecticut, Storrs, CT; Ashutosh Chilkoti, Dept. of Biomedical Engineering, Duke University, Durham, NC.

Three-dimensional micro- and nanostructures have significant potential for biomedical applications. In our studies, various approaches have been applied to fabricate 3-D structures. One approach uses masked ion beam lithography (MIBL), which simultaneously modifies both the surface topography and chemistry. Spin cast PMMA films were submitted to Ca^{+} ion and P^{+} ion implantation. Arrays of holes with nanoscale depth and microscale width were generated, and surface hydrophobicity was modified during the process. The effect of ion implantation on cell attachment was evaluated by culturing osteoblast cells on the substrates. The other approach used was UV polymerization to fabricate patterns. The bottom layer of the structure consists of biocompatible polymers bearing adhesion-promoting peptides or growth factors. The surface was patterned with various monomers by irradiating UV through a projection mask. A structure consisting of a nonbiofouling surface with bioactive channels was achieved. It is also possible to build multiple layers through this technique. Alignment of fibroblast cells and extracellular matrix formation is the end objective. In a modified approach, we have shown that an amphiphilic comb polymer film with short oligoethylene glycol side chains appended on a MMA backbone can be used as a physico-chemical barrier to constrain cells on substrates. Microcontact printing the comb polymer on a substrate and then backfilling the unpatterned regions of the substrate with a cell adhesive protein fibronectin (FN), or vice versa, created highly resolved micropatterns of cells in 10% serum for up to a month in culture. AFM of the microstamped surfaces indicated 3D like nanostructures. All these methods might provide routes to control the interaction of cells with diverse substrates for applications in biomaterials and biotechnology.

4:30 PM H9.7

BIO-INSPIRED SELF ASSEMBLY OF MICRO- AND NANO-STRUCTURES FOR SENSING AND ELECTRONIC APPLICATION. H.McNally, S.W. Lee*, D. Guo*, M. Pingle*, D.

Bergstrom*, R. Bashir*, School of Electrical and Computer Engineering*, Department of Medicinal Chemistry*, Department of Biomedical Engineering*, Purdue University, W. Lafayette, IN.

Bio-inspired assembly, through the use of bio-molecules such as DNA and proteins, will play a critical role in the advancement of novel sensing techniques and for the realization of heterogeneous integration of materials. For many of these applications, such as antibody-based biosensor and the study of controlled cell growth, DNA and protein patterning techniques are crucial. We will present an update of our work on protein patterning techniques using microelectronic fabrication, DNA hybridization and biotin-streptavidin pairing. Fluorescein conjugated streptavidin and Anti-Listeria Antibodies were patterned as a demonstration. To show its application in biological inspired self-assembly, this technique was used successfully in the self-assembly of 20 nm streptavidin conjugated gold particles. In addition, the integration of nano- and micro-scale heterogeneous materials is very important for novel material synthesis and electro-optic applications. We will present an update on our work to assemble silicon electronic devices using DNA/charged molecules and electric fields. Device are fabricated, released, charged with molecules, and subsequently manipulated in electric fields. Electrical properties of these devices including resistors and junction diodes are investigated after the assembly has occurred. The techniques described can be used to integrate the hybrid device such as nano- or micro-scale resistors, PN diodes, and MOSFETs on silicon or other substrates such as glass, plastic, etc.